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Review

Titanium Dioxide-Based Photocatalysts for Degradation of Emerging Contaminants including Pharmaceutical Pollutants

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Abstract: Contamination of the environment has been a growing problem in recent years. Due to the rapid growth in human population, the expansion of cities, along with the development of industry, more and more dangerous chemicals end up in the environment, especially in soil and water. For the most part, it is not possible to effectively remove chemicals through traditional remediation techniques, because those used in treatment plants are not specifically designed for this purpose. Therefore, new approaches for water remediation are in great demand. Many efforts have been focused on applications of photocatalysis for the remediation of chemical pollutants including drugs. Titanium(IV) oxide nanoparticles have particularly been considered as potential photocatalysts due to their favorable properties. In this article, we present the problem of emerging contaminants including drugs and discuss the use of photocatalysts based on titanium(IV) oxide nanoparticles for their degradation. A wide selection of materials, starting from bare TiO_2, via its hybrid and composite materials, are discussed including those based on carbonaceous materials or connections with macrocyclic structures. Examples of photodegradation experiments on TiO_2-based materials including those performed with various active pharmaceutical ingredients are also included.

Keywords: catalysts; degradation; pharmaceuticals; pollutants; titanium(IV) oxide

1. Introduction

The development of urban centers and economic growth is causing more and more damage to the environment by spilling various chemical substances into waters and soils. These compounds, now referred to as emerging contaminants, pose a significant threat because their presence affects negative changes in the environment. For a number of these substances, appropriate toxicological studies have been performed, allowing the identification of hazards. Various threats posed by the xenobiotics were considered as significant, especially toward aquatic organisms. The biggest industrial contributors to the pollution of the environment are fuel as well as the energy, chemical, metallurgy, wood, and paper industries. Compounds classified as emerging contaminants, which are also common industrial pollutants, are organic structures, mineral acids, salts (e.g., phosphates, nitrates, sulfates), heavy metals (e.g., cadmium, lead, copper, mercury), and other new substances, that are poorly documented for toxicology or even completely unidentified. However, it would be wrong to conclude that industry is the sole source of pollution. Wastes, even at low level concentrations appearing in ng × dm^{-3} to μg × dm^{-3} and coming from hospitals, agriculture, and animal production, pose a huge threat and impact the environment and human health. Among the pollutants present in wastewater, substances in daily use products are easily recognized. Namely, cosmetics, body care products (i.e., shower gels and shampoos from washing and bathing, cleaning products including surfactants, soaps, and detergents). Moreover, this also applies to hormonal substances, pesticides, dyes, carboxylic acids and their derivatives, high molecular weight compounds, aromatic compounds and their derivatives, phthalic esters, hydrocarbons, phenols, dyes, aromatic amines, and radioactive substances [1–4].

Many efforts have been focused on the application of photocatalysis for the degradation of chemical pollutants including drugs and the remediation of water. Titanium(IV) oxide, either in its mineral forms, dopant, or composite system, has been considered as a potential photocatalyst due to its favorable physicochemical properties. In this article, the applications of photocatalysts based on titanium(IV) oxide materials, starting from bare TiO_2, via its hybrid and composite materials for the degradation of emerging contaminants, including drugs, are presented.

2. Pharmaceuticals and Personal Care Products in the Environment

Pharmaceuticals and personal care products (PPCPs) including medicines, supplements, and cosmetic products have been widely studied for several years and are known to reveal differentiated biological activity [5]. Studies and reviews of Björlenius et al. [6], Halling-Sørensen et al. [7], Daughton and Ternes [8], and Jørgensen et al. [9] have presented and summarized most of the literature in this new and evolving field regarding the significance of medical substances and their impact on the environment. Some of these compounds have been identified as toxic to selected aquatic organisms [10–14] and edible tissues of plants [15], while some have accumulated in living organisms [8].

In the environment, PPCPs have been detected in surface, ground waters, and underground waters, which raises a serious concern. A grave threat is related to pharmaceuticals that belong to the following groups: antibiotics, anti-inflammatory drugs, analgesics, blood lipid regulators, cytostatic drugs, β-blockers, sympathomimetics, anti-inflammatory drugs, lipid regulators, vasodilators, antiepileptic drugs, and hormones that were detected in rivers and streams. An increase in domestic wastewater pollution is related to the rise in consumption of dietary supplements and drugs (non-prescription) by the population. The representative active pharmaceutical ingredients (APIs) that were found in wastewater include estrone, estriol, 17β-estradiol, testosterone, nadolol, metoprolol, pindolol, propranolol, terbutaline, salbutamol, diclofenac, ibuprofen, ketoprofen, naproxen, paracetamol, flurbiprofen, doxepin, imipramine, clomipramine, carbamazepine, sulfadiazine, sulfadimethoxine, sulfachloropyridazine, sulfamazine, sulfamethazine, sulfamethoxazole, sulfapyridine, sulfathiazole, enrofloxacin, trimethoprim, atenolol, and lincomycin. Besides pharmaceuticals, many personal care products also pose a threat to the environment such as fragrances, bactericides (disinfectants), insect repellents, preservatives, and sunscreen ultraviolet (UV) filters. The high incidence of these substances in the environment is a consequence of consumption and improper disposal [16,17].

Despite regulations regarding the use and utilization of PPCPs, their consumption is still very common due to a lack of alternatives or irreplaceability in everyday life. The contamination status of the environment including soil, surface waters, sludge, sediments as well as the related harmful effects to animals and humans has been broadly discussed by many authors, who have indicated relevant issues appearing in different regions of the world [18–21]. There are numerous reports on the ecotoxicological effects of personal care products (PCPs) [22], the occurrence of emerging organic contaminants in groundwater [23], environmental behavior and control technologies of PPCPs [19], occurrence, and removal of transformation products of PPCPs as well as illicit drugs in wastewaters [24,25]. One of the most critical threats is the seepage of PPCPs deposited in landfills into surface water and groundwater [26]. Fortunately, over the years, critical issues regarding the effects of PPCPs on human and ecological health have been identified, along with the increase in public awareness on this subject. Boxall et al. identified the top twenty priority questions to understand better and manage the risks of PPCPs [27]. They presented these questions in the form of seven categories, indicating the issues related to prioritization of substances for assessment, possible exposure pathways, bioavailability and uptake, characterization of effects, risk and relative risk, resistance toward antibiotics, and risk management.

PPCPs as pollutants can be found in the environment in all regions of the world, in the sea and in surface waters, wastewater effluents, and drinking water (Figure 1). Ternes and Joss [28], Ternes et al. [29], and Zuccato et al. [30] all raised the issue concerning the identification of pharmaceuticals in the aquatic environment. The following APIs were identified and analyzed: bezafibrate, clofibric acid, naproxen, triclosan, trimethoprim, furosemide, caffeine, trimethoprim, phenazone, tolfenamine, simvastatin, sildenafil, gemfibrozil, fenofibrate, diclofenac, paracetamol, salicylic acid, and the carbamazepine drugs venlafaxine and nimesulide. The human body is only partially able to metabolize some of these pharmaceuticals, some are excreted unchanged or in the form of conjugates. It was also found that some pharmaceuticals are often irresponsibly disposed of in toilet bowls after their expiration date [29]. These metabolites and expired drugs ultimately reach wastewater treatment plants.

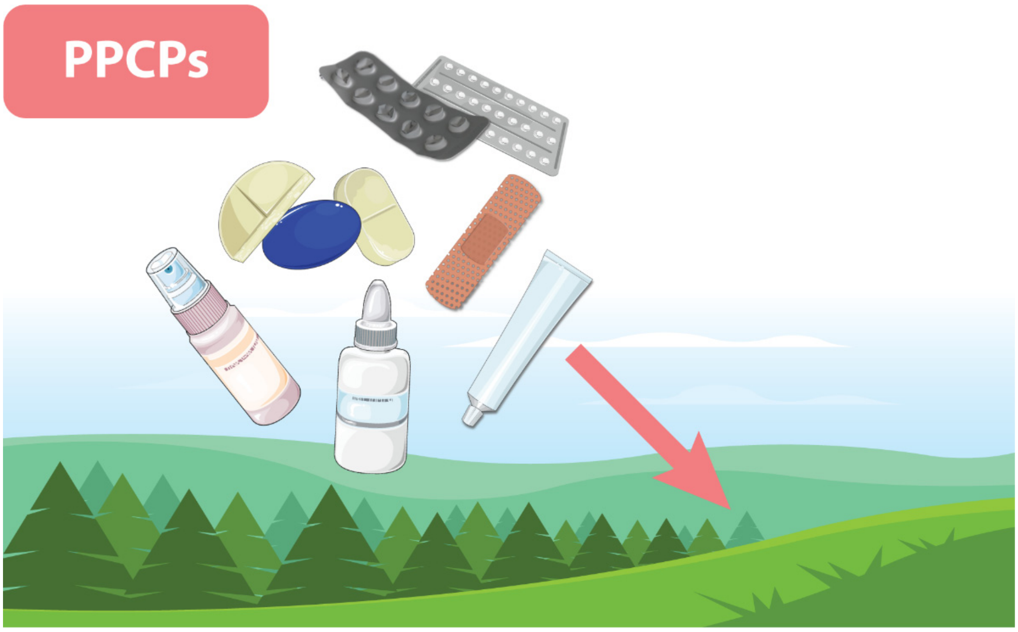

Figure 1. Pharmaceuticals and personal care products in the environment; PPCPs—pharmaceuticals and personal care products.

3. Remediation Techniques with the Use of Nanoparticles

Remediation facilities and therein applied techniques have revealed various effects toward specific PPCPs. It is important to note that the problem is a global one to which we, in European Union countries, are not immune.

Studies concerning PPCPs carried out in Greece [31] showed that during purification processes in a municipal wastewater treatment plant, the removal efficiency varied for individual compounds. These included purification processes such as screening and grit-removal followed by chemical ($FeClSO_4$), mechanical (sedimentation), and biological (nitrification, and denitrification) treatment. Only ten out of thirty-two pharmaceuticals were removed with relatively high ca. 80% efficiency including analytes such as paracetamol, salicylic acid, and lincomycin. Moreover, some substances were removed much less effectively, moderately, or only slightly. This was particularly observed in active pharmaceutical ingredients (API) such as carbamazepine, metoprolol, venlafaxine, ciprofloxacin, and simvastatin. The concentrations of fourteen pharmaceuticals, six hormones, two antibiotics, three PCPs, and one flame retardant were studied in two conventional wastewater treatment plants in South Korea by Kim et al. [32], wherein several PPCPs were detected in raw water at low concentrations. Many other studies have raised the issue of numerous PPCPs in different water sources including reservoirs, treated wastewater, surface and groundwater as well as tap water intended for human consumption in places such as Canada, Finland, France, Germany, Italy, and the USA [33–35]. The situation is in fact much worse in the case of dispersed on-site sewage treatment facilities, as shown in findings presented by Kuczyńska and Janica [36].

Communal and on-site wastewater treatment plants (WWTPs) were originally designed for the removal of organic matter and suspended solids, and in some cases—nutrients (total nitrogen and total phosphorus) to meet minimum discharge standards (e.g. biochemical oxygen demand—BOD). Remediation facilities are generally not designed for the removal of pharmaceuticals. Therefore, following various reports, pharmaceutical pollutants have been removed with varying degrees of effectiveness [17,37–44]. Given the above, there is an increasingly urgent need to search for and implement new methods and technologies to purify sewage using newly developed state-of-the-art analytical methods (Figure 2).

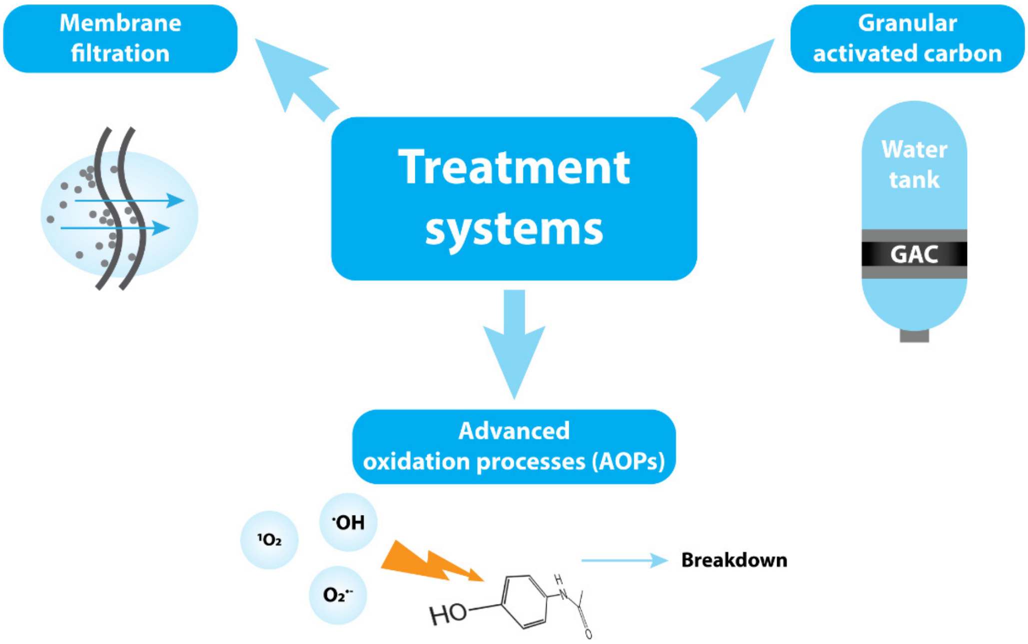

Figure 2. Treatment systems for the removal of individual pharmaceuticals.

Issues related to the occurrences and removal of PPCPs in drinking and sewage waters, analyses of their effects on health, and possible removal techniques have been reviewed by Yang et al. [25] and presented in original works by Vieno et al. [39]. They discussed many control strategies for PPCP contamination and advanced treatment systems for the removal of individual PPCPs such as membrane filtration, granular activated carbon, and coagulation as well as advanced oxidation processes (AOPs) [25,39].

AOPs are among promising new technologies that can be useful in the degradation of organic compounds. Photodegradation is a process of degrading substances during exposition to visible light, often in the presence of a supporting substance called a photosensitizer [45,46]. Photodegradation by AOPs can be induced in different ways including photolysis, photosensitizer- and ROS-induced degradation [47]. Precisely, among AOPs, several types of reactions can be distinguished including photochemical processes with UV photolysis, the combined effect of UV/H_2O_2, UV/O_3, UV/H_2O_2/O_3, photocatalytic degradation in aqueous semiconductor suspensions, Fenton photoreactions as well as ultrasound processes, radiation processes with ionizing radiation, alone or in combination with O_3, H_2O_2 [48–51]. Semiconductor nanoparticles can be applied in AOPs as catalysts. They are activated by the light of different wavelengths from ultraviolet by visible light to near-infrared, depending on the energy band gap [52].

The process of photocatalytic oxidation can be influenced by various factors including the type of solvent, temperature, pH of the solution, type of photocatalyst, amount of dissolved oxygen, time, and light intensity. Photocatalytic nanomaterials can be categorized in terms of dimensionality from zero-dimensional nanoparticles with quantum dots via one-dimensional such as nanorods, nanoribbons, nanotubes to two- and three-dimensional such as graphene. Doping metal oxide (MO) nanoparticles (NP) or preparing their heterojunctions can also increase their photocatalytic activities in visible light [53].

Among the photosensitizers, MO NPs constitute an intensively studied group of substances for potential applications in the photo-remediation of pharmaceutical and environmental wastewaters. To the group of photocatalytic nanomaterials that have been applied for the treatment of wastewater belong titanium dioxide (TiO_2), bismuth ferrite ($BiFeO_3$), zinc oxide (ZnO), cupric oxide (CuO), graphitic carbon nitride (g-C_3N_4), and reduced graphene oxide (rGO). Various forms of core-shell nanoparticles can be distinguished such as spherical, nanomatryushka, multiple cores in a single shell, hexagonal, and movable cores with hollow shells [53–61]. However, other nanostructures have also been studied for these applications (i.e., silver halides, phosphates, metal sulfides (i.e., CdS), porphyrins (Pp), and their derivatives or carbonaceous materials like carbon nanotubes (CNT) and heteroatom doped graphene [62–65]). Interestingly, composites of two or more substances have demonstrated a synergistic effect in the improvement of their photocatalytic activities, which was presented for MO NP combined with various photosensitizers and carbon-based nanomaterials such as carbon nanotubes [66,67].

4. Physicochemical Properties of Titanium Dioxide and Its General Applications

Titanium(IV) oxide (TiO_2), often referred to as titanium dioxide or titania, commonly appears in nature in three mineral forms: (a) anatase, (b) rutile, and (c) brookite. Aside from naturally occurring forms, commercially produced forms are also available such as P25, which is a mixture of anatase and rutile (depending on the supplier, the ratio of anatase to rutile ranges between 80:20 and 70:30). Brookite is often overlooked due to lower photo-reactivity than that of other TiO_2 polymorphic forms. When used, it is usually prepared as a composite of anatase-brookite [68].

The broadness of TiO_2 applications comes from the desirable material properties such as non-toxicity, high photostability, low cost, and photocatalytic potential [55]. Many advantages of photocatalysis with titanium dioxide can be quoted, for example, the ease of its immobilization by coating, long-term chemical stability of the photocatalyst, promising photodegradation efficiency, and hydrophilicity, non-toxicity, low cost, high photo-reactivity. However, some disadvantages of titanium dioxide can also be noted, especially concerning the optical response of titania, mainly in the UV light range, and fast recombination of the generated electron-hole pairs. Both can be avoided by proper modification of the material structure [53,69]. Modifications of the titania catalyst aim to increase its activity and thus boost its reactivity in visible light. The TiO_2 band gap of 3.2 eV only allows the absorption of light with a wavelength below 387 nm, which barely falls within the visible light spectrum [70,71]. Therefore, various surface developing agents for use with titania as well as immobilization techniques of titania as a catalyst within the active phase of the reactors have been developed [53,72]. Some attempts have been made to modify TiO_2 photocatalysts by doping with metals and non-metals (nitrogen, sulfur) as well as by heterojunction with another semiconductor in order to extend the absorption wavelength toward the visible light spectrum and to limit the recombination of electron-hole pairs [69].

The relevant titanium dioxide is a semiconductor-based material, which after irradiation undergoes a three step photocatalytic reaction. Initially, the titania molecule absorbs a photon with energy higher or equal to the value of 3.2 eV and passes to an excited state in which electrons in the conduction band and holes in the valence band are generated. Furthermore, in order to complete a photochemical reaction, electrons react with electron acceptors (usually in the presence of co-catalyst) in reduction reactions, and donors in oxidation reactions. In this way, when we have reactions of photo-induced electrons and hole pairs with surrounding oxygen and water molecules, reactive oxygen species (ROS) are formed such as superoxide ($O_2{}^{\bullet -}$) and hydroxyl ($^{\bullet}OH$) radicals [73,74].

The TiO_2 photocatalytic process proceeds according to the following mechanism (based on Zhu et al. [75]):

$$\mathrm{TiO_2} + hv \rightarrow h^+ + e^- \tag{1}$$

$$O_2 + e^- \rightarrow \bullet O_2^- \tag{2}$$

$$H_2O + h^+ \rightarrow H^+ + \bullet OH \tag{3}$$

$$OH^- + h^+ \rightarrow \bullet OH \tag{4}$$

$$2 \bullet O_2^- + 2H^+ \rightarrow H_2O_2 + O_2 \tag{5}$$

$$\bullet OH + \bullet OH \rightarrow H_2O_2 \tag{6}$$

$$H_2O_2 + \bullet O_2^- \rightarrow \bullet OH + OH^- + O_2 \tag{7}$$

$$Substrate + \bullet O_2^- + \bullet OH \rightarrow CO_2 + O_2 + by\text{-}product \tag{8}$$

After receiving a quantum of energy in the form of photons, the energy of which is higher than the bandgap of TiO_2, the unpaired electrons from the valence band of TiO_2 migrate toward the conduction band (1). This leads to the formation of positively charged holes on the valence band (h^+). Next, the conduction band electrons travel toward the catalyst's surface where they interact with surface oxygen, leading to the formation of superoxide radicals ($\bullet O_2^-$) (2). Following the conduction band electrons, the positively charged holes (h^+) reach the surface and react with surface water (H_2O) and adsorbed hydroxyl groups (OH^-), leading to the formation of hydroxyl radicals ($\bullet OH$) ((3) and (4)). This leads to a cascade of reactions where newly created hydroxyl radicals react with each other, leading to the formation of hydrogen peroxide (H_2O_2) ((5) and (6)). Then, the created ROS species (7) interact with substrates, in this case, contaminants, leading to their degradation (8) [75–77].

In order to enhance the properties of photocatalysts and overcome their inherent limitations such as low light utilization, redox rates, and high recombination rates of electron-hole pairs; semiconductor photocatalysts are modified in different ways, leading to the formation of hybrid materials and composites. In these conjugates, two or more materials with different bandgaps are used, which leads to the formation of heterojunctions of different character. The most common types of these heterojunctions are type-II and Z-scheme while step-scheme (S-scheme) heterojunctions are also slowly becoming more and more common [78].

In the case of type-II heterojunctions (Figure 3), electrons that are situated on higher energetic levels on the conduction band migrate to another photocatalyst with a conduction band that has lower energetic level. This occurs when both photocatalysts in a system are exposed to light with sufficient energy to generate electron-hole pairs. Similarly, the generated holes in both photocatalysts follow a reverse migration, from a lower energetic level valence band to a higher one. This leads to the accumulation of electrons on one photocatalyst (PC II) and holes on the other (PC I), which in such a case act separately as a reductor and oxidizer, respectively. The recombination of electron-hole pairs is effectively suppressed due to this separation, which promotes better energy conversion rates in the photocatalytic system. However, the redox ability of these systems is limited due to the occurrence of respective redox reactions on photocatalysts with lower reduction and oxidation potentials [79,80]. Another type of heterojunction is the S-scheme heterojunction, which is similar in the mode of action to the aforementioned type-II heterojunction. The key difference between the two heterojunctions lies in the charge-transfer route. In the type-II heterojunction, the charge-transfer occurs within the same conduction and valence bands of the photocatalysts in the system. In the S-scheme heterojunction, the charge-transfer occurs between the conduction band with a lower energetic level of one photocatalyst and the valence band with a higher energetic level appearing on the other. Due to better charge separation, the redox reactions occur on the photocatalysts with either better reduction or better oxidation potential [78]. Traditional Z-scheme photocatalysts utilize redox pairs, and because of this, their utility is restricted to liquid phase solutions only. In order to overcome this limitation, all-solid-state photocatalysts equipped with an electron mediator (usually a noble metal like Ag, Au, or Pt), and direct Z-scheme photocatalysts without an electron mediator were developed [79].

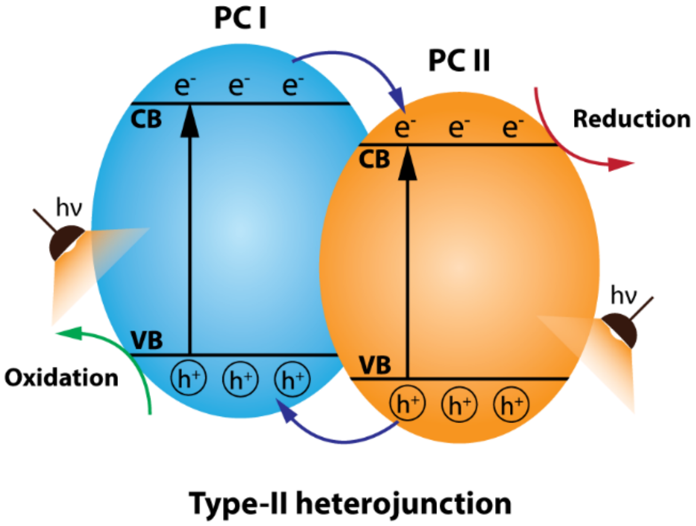

Figure 3. Representative charge-transfer route in the type-II heterojunction photocatalyst; CB—conduction band, VB—valence band, PC I—photocatalyst I, PC II—photocatalyst II (based on references [78,79]).

Titania is mainly used as a white pigment in the production of ceramics, cosmetics, paint, paper, pharmaceuticals, and electronics. TiO_2 has revealed many applications in pharmacy and medicine because of its photocatalytic properties and oxidizing activity. It is known as a European food additive E171 and, because of its high reflective index, has a common role as a pigment for pharmaceutical products. This molecule is used in sunscreens as a UVA and UVB blocker to diminish UV light penetration through the skin [81,82] (Figure 4).

Titania can be used as an antibacterial and antifungal agent. In dermatology, it was used in new methods of treating diseases such as acne and atopic dermatitis [83]. Gupta et al. evaluated TiO_2 and Ag-TiO_2 antibacterial properties against *E. coli*, *P. aeruginosa*, and *S. aureus* [84]. A different study reported that ROS resulting from UVA excitation of TiO_2 eradicated *E. coli*, methicillin-resistant *S. aureus*, and *C. albicans* fungi. The addition of sodium bromide increased this effect by up to 3 logs reduction (which means that the number of germs was 1000 times smaller) [85]. In another study, Ananpattaarachai et al. analyzed the antibacterial activity of Ni-doped and N-doped TiO_2 nanoparticles against *E. coli* and *S. aureus* [86]. The researchers observed the inactivation of both bacteria strains by N-doped and Ni-doped TiO_2. N-doped material showed better antibacterial properties than Ni-doped, mainly due to better sensitization toward visible light.

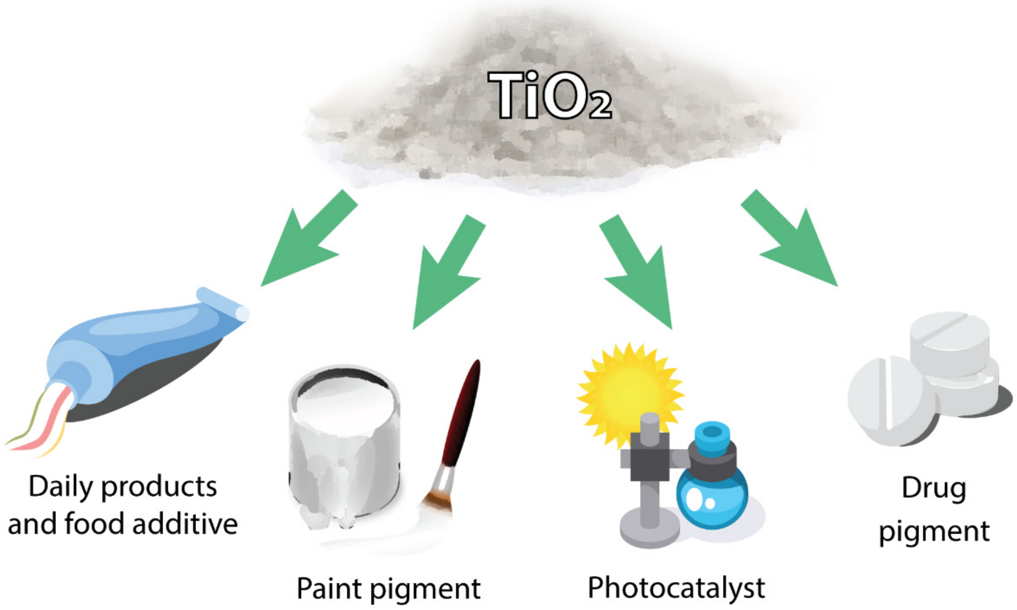

Figure 4. Titanium(IV) oxide and its broad applications.

Titanium dioxide is a biocompatible material and can be used in many sciences, industries, and medicine branches including stomatology and implantation technology. Nano-TiO_2 is a biocompatible material used to replace body tissues, as in through bone implants. Thanks to its biocompatibility, it can be used to reconstruct facial tissues and in dental implants—it also induces faster bone growth, improves the durability of implants, accelerates healing, and has anti-infective effects [87]. In the study carried out on mouse pre-osteoblastic cells MC3T3-E1 implanted on mineral matrix, Si-TiO_2 prominently meliorated expression of osteogenic differentiation genes. In in vivo tests in rat femur silicon doped titanium dioxide nanotubes compared to TiO_2 nanotubes and titanium implants enhanced durability of implant fixation by properly 18% and 54%, respectively. Moreover, Si-TiO_2 stimulated osteogenic differentiation of osteoblastic cells, which led to better integration of Ti with the bone structure [88]. In addition, Zane et al. studied the antibacterial action and biocompatibility of N-doped TiO_2 nanoparticles for use in dental resin formulation [89].

Many sensor properties of TiO_2 have been analyzed. Nanoparticles of TiO_2@ZnO and their hybrids with graphene oxide were studied as new drug delivery carriers for curcumin where the release of the load was pH-dependent [90]. Xin et al. created a photoelectrochemical sensor with nano-Au and self-doped TiO_2 nanotube arrays, which revealed the ability to detect kanamycin selectively [82]. Nanocomposites of polyaniline films with TiO_2 and RuO_2 nanoparticles on multi-walled carbon nanotubes were used for the electrochemical detection of epinephrine [91]. Nanorods of TiO_2 functionalized with quantum dots (CdS) were used as a substrate to confine glucose dehydrogenase for visible light-driven glucose oxidation and were used as part of the biocathode in a platform based on a cell visible light-driven biofuel [92]. In a different study, sensors based on carbon paste electrodes were prepared and modified by Ru-doped TiO_2 nanoparticles (from the liquid impregnation process). The sensor's task was to detect clozapine in pharmaceutical formulations and human urine [93]. Keshavarz et al. presented applications of self-assembled quantum scale structured (Q-structured) TiO_x in surface-enhanced Raman spectroscopy (SERS), which is a technique used in biomolecular detection of DNA, RNA, and proteins [94]. In order to overcome limitations of Raman spectroscopy and to perform the assay, a SERS template is necessary. The most commonly used materials in SERS are noble metals like Au and Ag. In the study, the researchers decided to prepare a biosensor based on a metal oxide in order to further develop the technique. The Q-structured TiO_x was prepared by multiphoton ionization. The material was self-doped, which led to the formation of additional oxygen vacancies that altered its electrocatalytic properties (i.e., the material band gap was lowered (2.11 eV compared to 3.2 eV in anatase)). Q-structured TiO_x templates were studied in a biosensor assay with three cell lines: fibroblast, HeLa, and breast cancer cells. The template was then used for the detection of EGFR, which is a common biomarker in breast cancer as well as for the preparation of SERS biomolecular fingerprint spectra in HeLa and fibroblast cells. The detection limit was as low as 1 nM with a maximum enhancement factor (EF) reaching up to 3.4×10^7. It is worth noting that this value was one of the best achieved for semiconductor templates and comparable with EF values achieved with noble metal SERS templates.

5. Titanium Dioxide as a Photocatalyst for Water Remediation Applications

Initially, TiO_2 was tested for applications in solar energy production. Later on, the studies evolved into environmental photocatalysis [55]. Titanium dioxide and its various modifications have been considered for applications in water remediation. In previous sections, we discussed the pros and cons of this material in depth. As a result of these, the most significant efforts have been targeted at research making TiO_2 an appropriate catalyst for photodegradation of common water contaminants including emerging contaminants. Most compounds belonging to this group are stable APIs that are difficult to remove from aqueous solutions. TiO_2 is not the sole material used for this application, and there are many alternatives among metal oxide nanoparticles and other materials such as quantum dots, which have found use in the photocatalysis of pharmaceutical water contaminants. Hooshmand et al. summed up these applications in their review that covered a broad selection of nanophotocatalysts for biomedical wastewater management [95]. Apart from pharmaceuticals, substances used in agriculture also belong to emerging contaminants and pose a significant threat when entering the environment in a non-regulated manner (Figure 5).

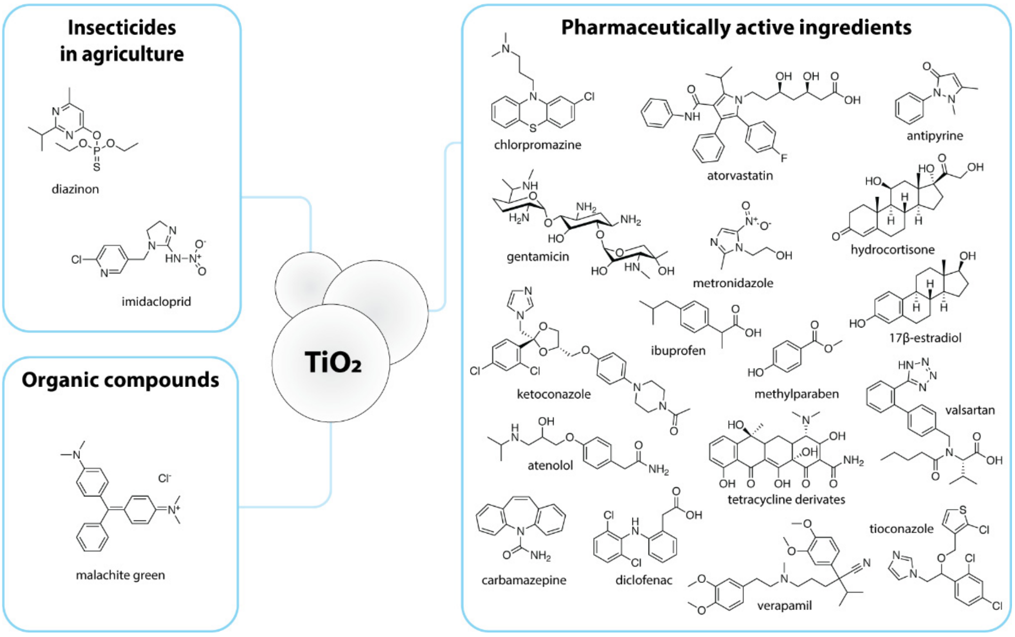

Figure 5. The applicability of TiO_2 as a catalyst in the photodegradation studies of various insecticides in agriculture, pharmaceutically active ingredients, and selected organic compounds including dyes.

In agriculture, TiO_2 NPs were applied in photocatalytic degradation of heterocyclic organic pollutants such as diazinon and imidacloprid, which are used as insecticides. The risk posed by these chemicals is associated with the fact that they can be washed from the soil into waterways, effectively contaminating the soil and rendering it unusable, or worse, posing a threat to human health if the pollutant enters drinking water supplies [96]. The results of the photocatalytic tests with titania indicated a 99% decrease in the initial concentration of 0.13 mM diazinon dissolved in 5 dm^3 of water after 100 min of irradiation with 287 nm UV light in the presence of H_2O_2. The authors stated that this rate could only be achieved with an optimal concentration of H_2O_2. Too low or too high concentrations could negatively impact the process of photocatalytic degradation. Moreover, it was found that H_2O_2 could promote the generation of $OH^{\cdot}$ radicals, and also, in abundance, it might act as a $OH^{\cdot}$ scavenger or react with TiO_2, forming peroxo-compounds. Conversely, it was found that 0.22 mM imidacloprid solution in 5 dm^3 of water was almost completely degraded using immobilized nanoparticles of titania after 90 min of irradiation with 267 nm UV light in the presence of H_2O_2 [96].

The ever-growing worldwide use of drugs corresponds with higher contamination of the environment, especially water. This is a significant concern and a challenge for modern society. With regard to the degradation of pharmaceutical pollutants in water, TiO_2 has been used thus far to catalyze photodegradation of drugs belonging to classes such as antibiotics, analgesics, anticonvulsants, β-blockers, lipid regulators, non-steroid anti-inflammatory drugs (NSAIDs), psychiatric drugs, and many more [97]. One of the studies on the matter presented an application of TiO_2 for the degradation of ibuprofen (IBP) in water paired with an ecotoxicological analysis of such a solution [98]. Researchers used artificially contaminated ultra-pure water as well as spring water. Tests were performed under artificial and natural UV light produced with a 125 W medium-pressure Hg vapor lamp, and the total radiation equaled 110.67 $J \times cm^{-2}$. The amount of IBP removed from the ultra-pure water solution containing 1000 $mg \times dm^{-3}$ TiO_2 and 1.0 $mg \times dm^{-3}$ IBP after 1 h of treatment with artificial UV light was 92% with a total organic carbon (TOC) removal rate reaching 78%. During the study, it was found that artificial UV light was more beneficial for the process. Concentrations of TiO_2 used in the tests varied between 20–1000 $mg \times dm^{-3}$, whereas the 1000 $mg \times dm^{-3}$ concentration proved to be the optimal one. Various control studies were implemented including a direct photolysis test of IBP under solar irradiation. These tests showed that the natural photolysis rate for IBP was minimal under 10% after 1 h of irradiation, which is consistent with the state of knowledge regarding the stability of IBP under light exposure [47]. In the sample filled with spring water, the efficiency of photocatalysis was influenced by minerals present in the water and negatively impacted the overall process. The achieved degradation rate of IBP and TOC removal, in this case, were 60% and 45%, respectively. Regarding the ecotoxicological studies, the treated solutions were tested against *Daphnia similis* and *Raphidocelis subcapitata*. Bioassays with *D. similis* showed 30% immobilization after 48 h of exposure. Tests with *R. subcapitata* at first showed enhanced growth for the samples after 5 and 10 min treatment followed by 40% growth inhibition for the sample after 45 min of treatment. The inhibitory effect gradually decreased with prolonged treatment of the solution. Thus, no inhibitory effect was observed in the sample after 120 min of treatment. The initial toxicity of IBP on these organisms was not tested [98].

In different studies, immobilized TiO_2 was applied in the UV light-induced photocatalytic degradation of three pharmaceuticals, namely, atenolol (ATL), chlorpromazine (CPR), and metronidazole (MET) in a water solution [99]. In the study, pure anatase (>99% anatase, 8 nm crystallites) immobilized on ceramic plates by the sol-gel method was applied. After 8 and 16 h, the TOC removal rates reached 70% and 90%, respectively. Ecotoxicological tests were performed on *Spirodela polyrrhiza* plants. The plants were grown in a medium containing 20 $mg \times dm^{-3}$ concentrations of each pharmaceutical without any prior photocatalytic treatment. Ecotoxicological assessments were made based on relative growth rate (RGR) and relative frond number (RFN). They resulted in the death of all plants after 24 h exposure in an untreated pharmaceutical mixture. What is interesting is that *S. polyrrhiza* exposed to the photocatalytically pre-treated mixture, retained their growth ability. Plants exposed to pharmaceutical solutions for 8 h revealed RGR and RFN loss of 28.57% and 30%, respectively, due to the presence of harmful intermediates in the mixture. Plants exposed to pharmaceutical solutions pre-treated photocatalytically for 16 h revealed no change in RFN and only a 2.37% loss of RGR. This observation proved that photocatalytic treatment of the pharmaceutical solution significantly reduced toxicity of the solution on tested plants [99].

In another study, a molecularly imprinted photocatalyst with low-TiO_2 loading was prepared for the degradation of different pharmaceuticals such as atorvastatin (ATR), diclofenac (DIC), ibuprofen (IBP), tioconazole (TCZ), valsartan (VAL), ketoconazole (KET), and gentamicin (GNT). The efficiency of photodegradation using a photocatalyst in non-imprinted systems and a commercial Degussa P25 TiO_2 were compared [100]. Molecular imprinting was undertaken to address one of the disadvantages of TiO_2, which is the low selectivity of heterogeneous photocatalysis to target contaminants. The molecularly imprinted systems were prepared by an acid-catalyzed sol-gel method using 150 mg sample of a pharmaceutical, 100 mg of $TiO_{2,}$ and tetraethoxysilane (45 mmol) with the addition of 0.2 M HCl in the volume ratio of 1:2. Titania was added 2.5 h after the reaction had been initiated. Later, the template was removed by slow heating. First, the drugs were tested for their ability to photolyze. The tests showed an average degradation rate of 5.6% for all tested substances under irradiation without a photocatalyst, which was considered negligible. Experimental samples containing 50 cm^3 of the pharmaceutical and 33 mg of the photocatalyst were placed into a bath reactor with airflow (6.5 $cm^3 \times s^{-1}$). The rate of photocatalysis was evaluated at two points: (1) 1 h incubation of a pharmaceutical in the reaction solution for initial adsorption to the system; and (2) degradation stage under UV irradiation (125 W Hg vapor lamp, 45 $W \times m^{-2}$). In the case of molecularly imprinted systems, it was observed for all tested drugs that the photocatalytic performance was enhanced in contrast to non-imprinted systems and bare P25 TiO_2. It was found that the imprinted systems revealed higher degradation efficiencies by the margin of 5–427% than their bare counterparts. The increase in performance was explained by the presence of cavities selective toward the tested pharmaceuticals. These sites enhanced interactions between the drugs and TiO_2. Additionally, in the recycling tests with diclofenac, the system retained 60% of its initial photocatalytic activity after seven catalytic cycles [100].

In a different study, a TiO_2 system was used for the removal of antipyrine (AP) by photodegradation in spinning disk reactors [101]. The disks were made of glass and imprinted with TiO_2 through a sol-gel method. It was noted that under optimal conditions, AP degraded completely after 120 min of irradiation. Additionally, no loss of efficiency of the photocatalytic disks was observed, even after 10 cycles. The photocatalyst was tested for its dark activity, but no change in AP concentration was noted. After the addition of H_2O_2, molecular degradation reached 12.6% of the initial AP concentration. In the UV irradiation test, AP was removed 76.4% in 120 min. UV/H_2O_2 and $UV/H_2O_2/TiO_2$ systems reached 93% and 95.9% degradation rates of AP, respectively. Analysis with neural network simulations proved that the initial concentration of H_2O_2 had the greatest impact on the efficiency of the reaction, and its optimal concentration was found to be at 1500 $mg \times dm^{-3}$ [101].

Photocatalytic systems based on P25 TiO_2 immobilized on lime glass were studied by Klementova et al. for heterogeneous catalysis of a number of pharmaceuticals and personal care products such as hydrocortisone (HCR), 17β-estradiol (ESR), verapamil (VRP) and three paraben derivatives (PB): methyl- (MePB), ethyl- (EtPB), and propyl- (PrPB) [102]. The concentration of the contaminants varied in these tests, ranging from 1×10^{-4} to 2×10^{-4} $mol \times dm^{-3}$ for VRP, HCR, and PB while ESR was prepared as a saturated solution at 25 °C. After 2 h of irradiation, only 6% of the initial concentration of HCR remained in the sample with a TOC mineralization rate of 69%. For ESR, almost the entirety of the drug was photodegraded, leaving only 2% of the initial ESR concentration in the sample with a 32% TOC removal rate. Degradation tests of VRP revealed that 18% of the initial concentration remained in the sample after 2 h of irradiation, and the achieved TOC removal rate was at 18%. PB derivatives seemed to be quite resistant to photocatalysis, especially MePB, which had a three times lower degradation rate compared to other PB derivates. For MePB, 2 h of irradiation led to 20% reduction only in the amount of substrate, while for the same irradiation time, around 50% of EtPB and PrPB was degraded. One of the main aims of the study was to compare the results of homogeneous catalysis with ferric ions and heterogeneous catalysis with titania. Although Fe(III) achieved overall better degradation rates of tested substances, TiO_2 revealed better mineralization rates, which is an essential factor in photodegradation. The photocatalytic process often leaves still harmful intermediates that can accumulate in solutions. A good photocatalyst should also be able to remove them in the process [102].

Liu et al., in their study, showed the effects of photocatalytic treatment of pharmaceutical wastes by TiO_2 nanopore array electrodes [103]. The MO was immobilized on electrodes to avoid problematic separation of TiO_2 powder from the treated solution after the procedure concluded. Next, the efficiency of such solution was evaluated in an experiment focusing on photocatalytic and photoelectrocatalytic degradation of substances belonging to the tetracycline (TCL) family, which is a group of antibiotics commonly used in agriculture and live stocking. The researchers used a three-electrode system, platinum, Ag/AgCl, and TiO_2 electrodes in the following conditions: 254 nm length UV light irradiation, 2.5 mW × cm^{-2} light intensity, 0.5 V current, pH 5.5, and 0.02 mol × dm^{-3} sodium sulfate as the electrolyte. The solution was stirred, and no air flow was applied in the photoelectrocatalytic and photocatalytic studies. In the latter case, no current was applied. TCL was applied in a 20 cm^3 solution at the 10 mg × dm^{-3} concentration. According to the results obtained for the nanopore array electrode, photoelectrocatalytic degradation allowed for the removal of 80% of TCL from the solution within 3 h. Nanofilm electrodes removed 55% of TCL content. The electrodes were tested under various conditions, allowing the occurrence of different mechanisms of degradation. Electrochemical, photocatalytic, and photoelectrocatalytic degradation rates were evaluated separately. Electrochemical degradation occurred at a negligible rate during the experimental time. In the sample under UV light exposure, 23% of TCL was degraded in 3 h. When both irradiation and current were applied, the removal ratio rose to 80%. During the course of the study, the electrodes proved to be effective for photodegradation; they had strong mechanical stability and were easy to separate from the solution. Therefore, TiO_2 nanopore array electrodes seem to constitute a promising material of photoelectrocatalytic potential for the removal of pharmaceutical pollutants from wastewater [103].

In a study by Haroune et al., carbamazepine and its derivates, carbamazepine epoxide (CBE), acridine (ACR), and acridone (ACO) were treated with TiO_2 (99% anatase) and ZnO NPs [104]. Additionally, the effects of environmental parameters (pH, ionic strength, natural organic matter content) on the efficiency of the reaction were evaluated. The catalytic efficiency varied by a large margin depending on the above-mentioned parameters as well as the treated derivate. The efficiency of TiO_2 was higher than that of ZnO in the degradation of CBZ and CBE, whereas no major changes in reaction efficiencies were observed in tests with ACR and ACO. The reaction parameters were tested, pH, and natural organic matter played a significant role in influencing the photodegradation of CBZ and CBE, which was not the case for the two other derivatives. The following materials were prepared for the tests: (a) NP suspensions—prepared by suspending 1 g of NPs in 1 dm^3 of MilliQ water; (b) 1 mg × cm^{-3} solutions of pharmaceuticals; and (c) formic, humic, and tannic acids—served as model substances for natural organic matter content. Experimental solutions consisted of a 400 µL aliquot of each pharmaceutical stock solution in 40 cm^3 NP suspensions in 50 cm^3 polypropylene tubes. The final concentration for TiO_2 and ZnO NPs was 500 mg × dm^{-3} and 10 µg × cm^{-3} for pharmaceuticals. Methanol content was measured to be under 1%. pH modifications were made by adjustments with either 0.1 M HCl or 0.1 M NaOH. Ionic strength was set by the addition of $CaCl_2$. Irradiation was performed with a 1500 W xenon lamp with irradiance reaching 735 W × m^{-2}. The wavelength produced was within the range of 300–800 nm. The reactions were performed in the following conditions: (a) 10 mM H_2O_2 was added to each sample; (b) irradiation time was 6 h; (c) temperature was kept at 35 °C; (d) three different pH values were used (3, 6.4, 11); (e) three different ionic strength parameters (0.01, 0.1 and 1M $CaCl_2$); and (f) three concentrations of humic and tannic acids (1, 10, 50 mg × dm^{-3}). At pH 6.4,

TiO_2 showed better photocatalytic rates than for ZnO in the photodegradation of CBZ. Transformation percentages for CBZ were as follows: 63% for TiO_2 and 35% for ZnO. For CBE, transformation rates reached even 80% for TiO_2 and 13% for ZnO. Following the authors' statement, the reason for the difference in degradation efficiency between TiO_2 and ZnO was unknown. At high pH, photodegradation of CBZ by TiO_2 was negatively impacted. This effect was also observed for ZnO. CBE photodegradation with ZnO occurred at higher rates both at low pH equal to 3 and at high pH equal to 11 than at pH 6.4. pH value revealed no effect on photodegradation of ACR. The model contaminants were also tested for degradation in dark conditions as well as in the presence of UV irradiation and in the absence of the photocatalyst, but no effect was noted. Ionic strength (IS) tests were made at pH 6.4. In the study, TiO_2 photodegradation rates increased with IS for CBZ, but this factor revealed no effect on the rates for CBE, ACR, and ACO. In the ZnO case, only in the sample where IS was the highest was the photodegradation rate of CBZ reduced. Similarly to TiO_2, IS had no effect on the photodegradation rates of CBE, ACR, and ACO. The effect of natural organic matter is difficult to evaluate because the reaction can be affected in two contrasting ways. Natural organic matter can either inhibit photodegradation by acting as a quencher or enhance it by acting as a photosensitizer [104]. Considering all the presented factors and their influence on the reaction environment, it is important to take into account all possible parameters when designing a photodegradation experiment [104].

Aside from pharmaceuticals, titania NPs have been applied for the UV-induced degradation of selected organic compounds including dyes. One of them was malachite green (MG), which is a synthetic dye commonly used in the leather and paper industries [105]. It was found that TiO_2 catalyzes step-wise N-demethylation of the MG dye, yielding N-demethylated MG species. In the study, it was possible to achieve up to 99.9% reduction in MG content with complete decolorization of the solution after 4 h of irradiation with 365 nm UV light. According to the study, TiO_2 was found to be an efficient photocatalyst in the removal of organic dyes in water solutions [105].

To sum up, titania has been applied for the degradation of synthetic dyes, APIs present in PPCPs as well as agricultural pollutants. Many photocatalytic systems have been studied where TiO_2 was used in different forms. In a number of examples, TiO_2 was modified to enhance its properties and overcome some of its shortcomings. However, simple modifications without the use of a dopant, co-catalyst, or a photosensitizer are limited in what they can offer. More complex systems based on titania, which are discussed in the next sections, are necessary to enrich titania in additional properties like photoactivity in visible light and improved charge transfer.

6. Titanium(IV) Oxide Modified by Doping or in Heterojunctions with Other Metal Oxides as a Photocatalyst for Water Remediation Applications

One of the drawbacks in applying a pure TiO_2 as a photocatalyst is the requirement to use near-UV irradiation to effectively induce the process of photocatalysis in the reaction environment. This limitation stems from titania's band gap: 3.2 eV for anatase and 3.0 eV for rutile. The required irradiation wavelength constitutes only 4% of visible light and falls well into the UV spectrum [71], rendering irradiation with visible light highly inefficient. However, this disadvantage can be overcome by a number of measures, especially by creating hybrid or composite materials with compounds that increase TiO_2 photosensitizing potential towards visible light. Titania's photocatalytic properties can be further enhanced by doping with other compounds. In particular, modifications of TiO_2 with noble metal ions can lead to satisfactory results in terms of photoconversion. Such doped materials with a broad band gap could be excited with visible light and thus could be considered as catalysts for photoremediation in visible light (Figure 6).

The reviewed materials were divided into two categories: single-doped—when only one dopant was used, and multi-doped—when more than one dopant was used. In the graph below (Figure 7) are presented admixtures for TiO_2 and representative catalytic decomposition processes in which they can be applied.

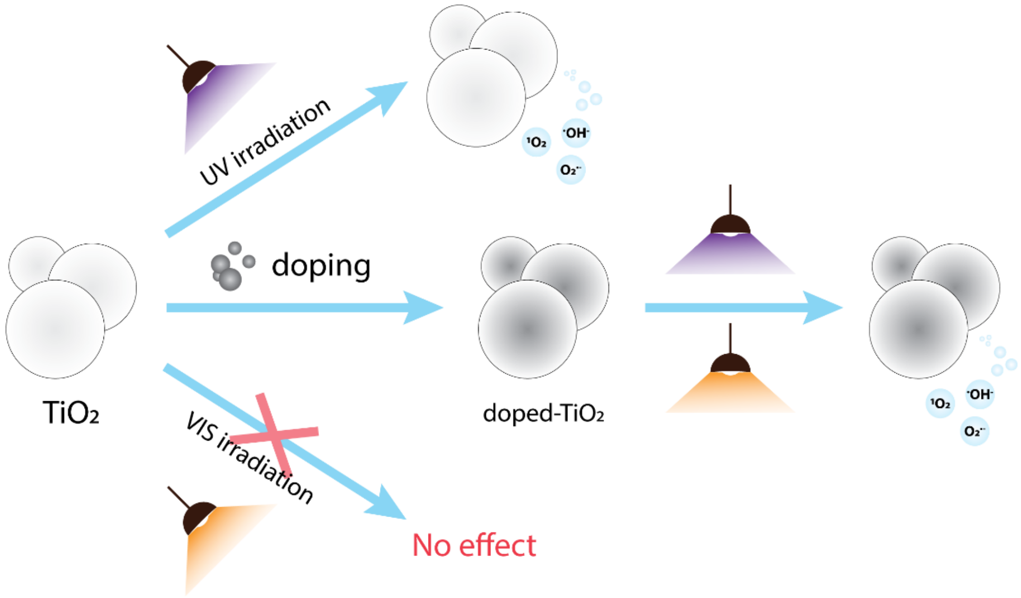

Figure 6. Graphical explanation of TiO_2 doping for water remediation.

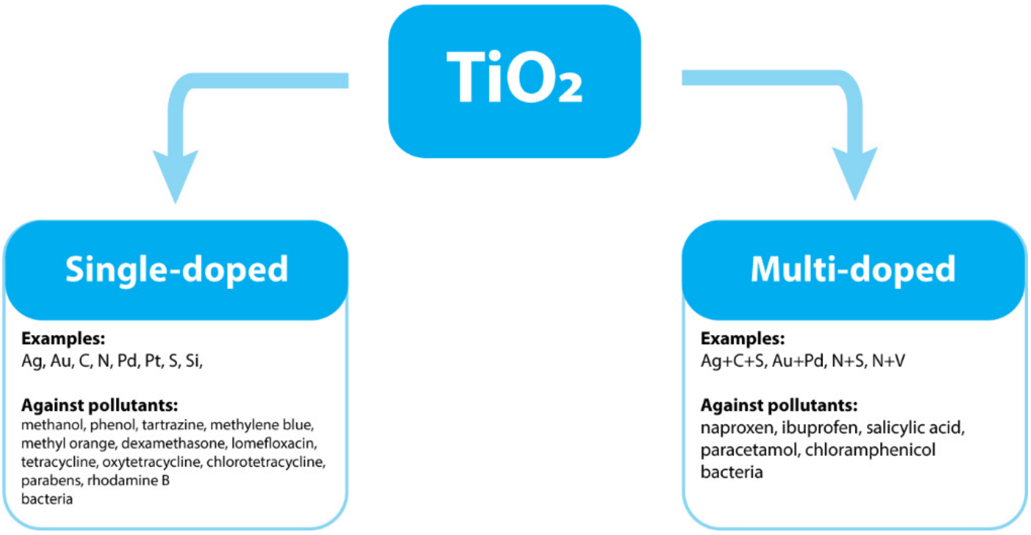

Figure 7. Possible modifications of TiO_2 with other atoms and substances that are decomposed due to the catalytic properties of obtained composites.

6.1. Single Atom Doped TiO_2 Composites

Within single-doped titania composites, various examples of non-metal doped (nitrogen, silica, sulfur, carbon) as well as noble metals-doped materials including silver, platinum, gold, and palladium can be discussed. These materials have been studied as photocatalysts for the degradation of chemical and pharmaceutical pollutants and bacteria (Figure 8).

In the study presented by Guo et al., the preparation of Si-doped molecularly imprinted titania photocatalyst and its application toward antibiotic degradation in wastewater was presented [106]. It was found that Si-TiO_2 showed a higher degradation rate of oxytetracycline under UV light produced by a xenon lamp than bare TiO_2 nanoparticles. Si-TiO_2 material was prepared by liquid phase deposition and later appropriately characterized. Interestingly, samples with Si-doped TiO_2 showed an 80.79% degradation rate of oxytetracycline after 120 min of irradiation. Reusability tests showed that the material could be re-used, as even after five cycles of degradation, the rates were at a relatively high level of 65.6% removal of initial oxytetracycline concentration. In another study by Daghrir et al., N-doped TiO_2 photodiodes with different nitrogen content were prepared using a radio frequency magnetic sputtering process to tune their optical absorption for activity in visible light [107]. These anodes were used in photo-electrochemical degradation of chlortetracycline in wastewater and allowed even for a 99.6% degradation rate after 180 min of irradiation with visible light and current intensity of 0.6 A. In a different study, N-doped TiO_2 photocatalysts were synthesized via the sol-gel method from titanium butoxide in the presence of guanidium chloride, which served as an N source [108]. In contrast to other studies, the prepared material was not in the form of pure anatase or P25, but as a mixture of anatase and rutile (about 40:60 anatase/rutile ratio, depending on the loading), making it a mixed phase material. The photoactivity of the photocatalyst was measured by photodegradation of 10 mg × dm^{-3} methylene blue (MB) water solution under visible irradiation with a fluorescent lamp (112 W and 3.2 mW × cm^{-2}). Photocatalysts with varying ratios of N/Ti were used. The material with 1:1 N/Ti loading proved to be the most efficient and showed up to a 97% degradation rate of initial concentration of MB after 100 min of irradiation with visible light [108].

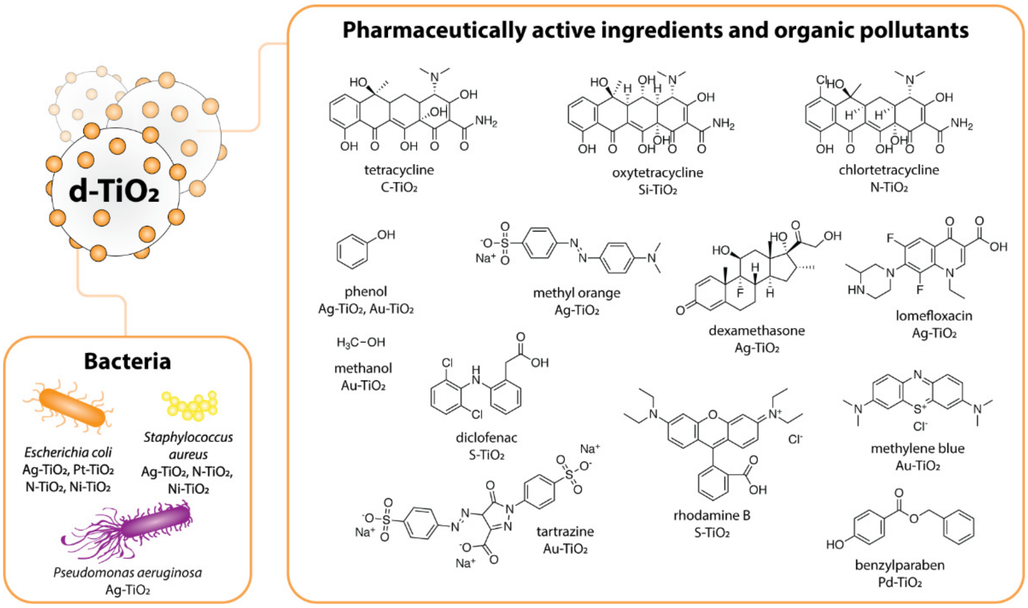

Figure 8. The applicability of single-doped titania composites as catalysts in the photodegradation studies of chemical and pharmaceutical pollutants and bacteria; d-TiO_2—doped titanium(IV) oxide.

Carbon-doped TiO_2 nanophotocatalysts were prepared by Ma et al. from TiO_2, starch, and γ-Fe_2O_3 by facile calcination and acid etching process [109]. C-TiO_2 photoactivity was tested by the photodegradation of tetracycline (TCL) water solution at the concentration of 10 mg × dm^{-3} under visible light irradiation. Five samples of the C-TiO_2 photocatalyst were used during the test. The samples were differentiated by starch content pre-calcification and contained either 1, 2, 3, or 5 g of starch, which acted as the C source in the material. Sample C-TiO_2-2 showed the highest photocatalytic activity, reaching 90.8% reduction in TCL in the solution after 160 min of irradiation with visible light (source of the light not described). The photoactivity of the novel material was significantly higher than that obtained for bare TiO_2, which reached only 30.4% reduction in TCL under the same conditions. In addition, the material showed high reusability, because after five cycles, its photocatalytic activity decreased only by 8.7% between the first and the fifth cycle. The difference between photoactivities of the composite material and bare TiO_2 was attributed to higher specific surface area of C-TiO_2, better light harvesting ability, and effective separation of photogenerated carriers [109].

Yi et al. prepared amorphous, sulfur-doped TiO_2 photocatalysts from tetrabutyl titanate by the sol-gel method with low-temperature calcination using thiourea as a sulfur source [110]. The researchers used three different calcination temperatures (300, 350, 400 °C) to produce three different photocatalyst samples, which were then applied in the photocatalytic tests. Photocatalytic activity was measured by the photodegradation of 10 mg $\times$ dm^{-3} diclofenac (DFC) in water under irradiation from white LED lamps. Out of the three materials and bare TiO_2, only the sample prepared at the 300 °C temperature revealed notable photoactivity. S-TiO_2 (300) degraded 93% DFC after 4 h of irradiation with visible light. Additional tests for S-TiO_2 (300) were performed wherein the influence of different light intensities, photocatalyst concentrations, and pH values were evaluated. The light intensity study showed that photoactivity improved with a stronger light source. LED lights were comparable to a 15A Xe lamp, with the highest photoactivity achieved for the 25A Xe lamp. As for other tests, the photoactivity of the material increased along with higher concentration of the photocatalyst (initial—0.2 g $\times$ dm^{-3}, up to 0.8 g $\times$ dm^{-3}) and decreasing pH (pH 6–11 range, the best results were noted for pH = 6) [110]. In a different study, sulfur-doped anatase TiO_2 was used for the degradation of rhodamine B (RhB) in an aqueous solution under a 300 W Xe lamp with a 400 nm cutoff filter that acted as a visible light source [111]. The photocatalyst was prepared by low-temperature hydrothermal oxidation of titanium disulfide in deionized water. As a consequence of sulfur doping, the composite's band gap was lowered from 3.2 eV to 2.65 eV, allowing for irradiation with visible light. For the degradation tests, a standard concentration of 10 mg $\times$ dm^{-3} was used for the model contaminant and 1 g $\times$ dm^{-3} concentration of the photocatalyst. Two samples of the photocatalyst were studied against two blank samples and pure TiO_2. The main difference between photocatalyst samples was the synthesis process and temperature. The first sample, ST-120-4, was prepared by a hydrothermal method carried out in 120 °C for 4 h. The second sample, ST-550-10, was prepared by the oxidation of TiS_2 in air at 550 °C for 10 h. According to the results, the sample ST-120-4 presented the best photodegradation rates with 80% removal of RhB in the solution after 60 min of irradiation with visible light. ST-550-10 showed a 50% removal rate after the same time in the same conditions. The authors pointed out that the difference between removal rates of both samples stemmed from different surface areas of the material, for ST-120-4, this value was notably higher [111].

Among the noble metal-doped titania, a significant amount of research refers to silver-modified TiO_2. Silver nanoparticles (AgNPs) present a high catalytic activity with optical properties that can be easily modified by changing their size and shape. AgNPs appear to be very promising in chemical and biosensing applications. As reported, conjugates of TiO_2 and Ag nanoparticles have revealed better photocatalytic activity under UV and visible light than each component separately. Conjugates of Ag with TiO_2 also presented better adsorption to microorganisms, which resulted in significant, up to 70-fold higher, bactericidal activity [56]. Photocatalytic activity of Ag-modified TiO_2 was tested by measuring the degradation rate of phenol in water solution under UV and visible light irradiation generated by a 1000 W xenon lamp. Two commercially available forms of TiO_2, P25, and ST01 (pure anatase) were loaded with AgNPs at 0.5, 1, and 2 wt.%. Unmodified P25 degraded 33% of phenol after 60 min of irradiation with UV light and 22% under irradiation with visible light. Better results were obtained for Ag-loaded TiO_2. For 2 wt.% Ag-P25, the highest degradation rate of phenol at 92% under 60 min UV irradiation was observed. Overall degradation rates in visible light were significantly lower for both materials modified and unmodified. It turns out that the 1% Ag-P25 sample achieved the best results under visible light irradiation when compared to other examined TiO_2 photocatalysts in the study including both unmodified and Ag-modified ST01. After 60 min of irradiation with UV light, only 23% of phenol content was degraded and 15–17% when it was irradiated with visible light at the same time. The study proved that Ag loading does not have a palpable effect on the photocatalytic activity of modified ST01 under UV light. For visible light, 2% Ag-ST01 was marginally more active than other loadings [56]. In the study presented by Yu et al., a composite material of TiO_2 nanotube (NT) arrays and silver particles was prepared in the form of $Ag/AgCl/TiO_2$ [71]. This composite material was obtained by depositing AgCl NPs on self-organized TiO_2 nanotubes and partial reduction of Ag^+ ions from AgCl after irradiation with a xenon lamp to Ag^0 species. The composite, as reported by the researchers, exhibited higher photocatalytic activity when irradiated by visible light. This rise in its activity was explained by plasmon resonance and charge separation effects. Electrons from Ag were excited by plasmon resonance and transferred to TiO_2 conduction band and, simultaneously, compensative electrons were transferred from Cl^- back to AgNPs. The material's efficiency was tested by photocatalytic degradation of methyl orange in water. The photocatalytic activity was compared with amorphous and anatase TiO_2 NT arrays, which did not show any photocatalytic activity under visible light. Additionally, the composite was studied against another reference photocatalyst, N-doped TiO_2 NTs. AgCl-TiO_2 presented insignificant photoactivity in visible light. Only after Ag^0 was deposited on the surface of the composite material could it be excited by visible light [71].

A noteworthy study where Ag-TiO_2 was used for the photodegradation of dexamethasone in wastewater was shown by Pazoki et al. [112]. Ag-TiO_2 was prepared with the modified photodeposition method. Researchers carried out experiments using different concentrations of Ag-TiO_2, dexamethasone, and hydrogen peroxide. Additionally, the influences of pH and temperature were analyzed during the study. In optimal conditions, dexamethasone photodegradation levels achieved for UV and visible light were 82.3% and 71.5%, respectively. In another study by Kulkarni et al. [113], Ag-doped TiO_2 was used in the photodegradation of lomefloxacin under UV-light produced by a mercury lamp. Materials were synthesized by liquid impregnation method in two concentrations—1% and 2%. According to the results, 2% Ag-TiO_2 revealed better degradation rates of lomefloxacin than pure TiO_2 and 1% Ag-doped particles. The achieved degradation rates reached up to 95% after 1 h of irradiation [113].

Au-doped titania has been broadly studied as a photocatalyst for its applications in the removal of water pollutants. A review on this subject was presented by Ayati et al. [114]. Gold as a noble metal on its own has poor reactivity. However, this is not the case for its nanoparticles, especially when their size falls below 5 nm. Gold nanoparticles are stable, rather non-toxic, and biocompatible, which fits with the TiO_2 physicochemical properties. Au-TiO_2 nanoparticles have so far been applied in the decomposition of methanol [115] and degradation of phenol [116], methylene blue [117], methyl orange [118,119], tartrazine [120], and various other organic dyes. Notably, while a rise in photoactivity of doped nanoparticles is usually observed for reactions where some chemical groups are present, the same photocatalyst can exhibit poorer activity than expected [114]. Gomes et al. presented a broad study on the detoxification of parabens using UV-A enhanced by noble metal-TiO_2 supported photocatalysts [121]. In the study, titania doped with either palladium, platinum, silver, or gold were used in the degradation of a paraben mixture containing methylparaben, ethylparaben, propylparaben, butylparaben (BuPB), and benzylparaben (BePB). Au-TiO_2 was prepared by the sol-gel method, for another photocatalyst, 0.5 w/w% noble metals were photodeposited on the TiO_2 surface after UV-induced reduction in precursor ions. The paraben mixtures were prepared by mixing 10 mg × dm^{-3} of each paraben in ultrapure water. The results of the photodegradation test with Au-TiO_2 were analyzed against photolysis rate (4%) and compared with bare TiO_2. For all photocatalysts, the presence of noble metal dopants improved the rate of paraben degradation compared to bare TiO_2. Ag and Pd co-dopants proved to be the most effective, achieving over a 50% reduction rate in initial paraben concentration after 180 min of irradiation. Pd-TiO_2 led to 75% reduction rate in BePB. TOC and COD (chemical oxygen demand) removal rates were also studied. Initial TOC and COD values for the paraben mixture were 35 mg × dm^{-3} and 95 mg × dm^{-3}, respectively. The best results were achieved with 0.5% of Pd-TiO_2 for which the mineralization rate was 25% and 19% for COD removal. Interestingly, Au-TiO_2 revealed the lowest activity among other noble metal photocatalysts in the study on the photodegradation of parabens. Supplemental toxicity assessment tests were carried out in the study on *Aliivibrio fischeri*, *Corbicula fluminea*, and *Lepidium sativum* species. Acute toxicity test was carried out on *A. fischeri* after 15 and 30 min of exposition to non-treated and treated samples. Bioluminescence inhibition rate was above 80% for all samples, showing that degradation rates achieved after 3 h of photocatalytic treatment were insufficient to lower the toxicity of the paraben mixture. However, toxicity tests with other species showed positive results. *C. fluminea* and *L. sativum* were more resistant species than *A. fischeri* and were used to assess the toxicity of samples pre-treated with the three most efficient noble metal photocatalysts (Pt-TiO_2, Ag-TiO_2, and Pd-TiO_2). A reduced toxicity in pre-treated samples against those species was found. Growth index of *L. sativum* increased from 40% to 70% after treatment with Pd-TiO_2, and to around 60% for other doped TiO_2. Mortality of *C. fluminea* clams decreased from 100% to 21% for the sample pre-treated with Ag-TiO_2 and was significantly lower for the other two photocatalysts. All in all, 0.5% Ag-TiO_2 and Pd-TiO_2 proved to be the most effective photocatalyst in the study for the removal of parabens from wastewater [121].

In the study presented by Murcia et al., gold and platinum nanoparticles were deposited on TiO_2 and used for the elimination of *E. coli* from urban wastewaters [122]. All prepared noble metal photocatalysts showed bactericidal effects better than the bare commercial P25 TiO_2. The potential was evaluated for different light intensities and the light intensity of 120 W $\times$ m^{-2} revealed the highest elimination rates of *E. coli* from wastewater. In the study, a 300 W solar lamp was used with an emission spectrum similar to natural light and mainline radiation at 365 nm. The reaction solution was constantly stirred with airflow. The optimal concentration of photocatalyst of 1 g $\times$ dm^{-3} was chosen as the optimal concentration for photochemical treatment of bacteria based on the authors' previous research. The tests were repeated three times in order to ensure reproducibility. The achieved margin of error was 0.1%. Reaction time was set at 5 h. The samples were incubated outdoors for 24, 48, and 72 h to check for bacteria regrowth. The turbidity of the samples was reduced to half of the initial value. The following various light intensities, 30, 60, and 120 W $\times$ m^{-2} were also studied. The highest CFU $\times$ cm^{-3} reduction was achieved for 120 W $\times$ m^{-2} light intensity. In tests without the photocatalyst, no complete removal was achieved even after 5 h of irradiation. In the presence of a 2 wt% Pt-TiO_2 and at 120 W $\times$ m^{-2} light intensity, all bacteria (*E. coli*, total coliforms, and other *Enterobacteriaceae*) were eliminated after 3 h of irradiation and no bacterial regrowth was detected even after 72 h. In tests, where light with the intensity of 120 W $\times$ m^{-2} was used for the given irradiation time, it was possible to completely remove *E. coli* species and most of the other accompanying bacteria. Addition of the photocatalyst allowed us to remove a higher number of remaining bacterial contamination in the sample. It is worth noting that in the case of irradiation with such a high light intensity, temperature increase (up to 57 °C) within the reactor also contributed toward the total bactericidal effect. The authors performed a recycling test of the photocatalyst and found that there was no loss of photoactivity of the photocatalyst after three cycles of the reaction [122].

6.2. Multiple Atom Doped TiO_2 Composites

Multiple-doped titania materials consist of titania that has been doped, for example, with nitrogen and sulfur, vanadium and nitrogen, gold and palladium as well as silver, carbon, and sulfur. The photocatalytic properties of these materials were studied toward the degradation of pharmaceutical pollutants in water and/or bactericidal activity (Figure 9).

Hamal et al. presented TiO_2 NPs co-doped with multiple atoms [123]. In the study, titanium oxide was doped with silver, carbon, and sulfur, which led to a composite Ag/(C,S)-TiO_2 with enhanced bactericidal and sporicidal activities. Various silver loadings were used—0, 0.5, 1, 2, 10, and 20 mol%. Carbon and sulfur co-dopants seem to further enhance photocatalytic and bactericidal properties compared to regular Ag-TiO_2. Properties of Ag/(C,S)-TiO_2 were evaluated in tests of gas-phase acetaldehyde degradation as well as *Escherichia coli* and *Bacillus subtilis* inactivation. These co-doped Ag/(C,S)-TiO_2 particles showed significant antimicrobial activity, even without additional irradiation, against both strains. An antibacterial test was conducted by suspending bacterial spores and cells in a vegetative state in water. According to the results, 10% Ag/(C,S)-TiO_2 exerted the best bactericidal effect on *E. coli* out of all samples tested with 8.9 log reduction after 30 min of exposure. Compared to bare P25 TiO_2 with 3.2 log reduction, it was a notable improvement. Authors pointed out that the presence of co-dopant silver and carbon played a major role in enhancing TiO_2 antibacterial properties. Results of the tests on *B. subtilis* were similar. A better bactericidal effect was achieved for doped-TiO_2 than bare TiO_2. In addition, higher loadings of Ag led to improved antibacterial activity [123]. Eswar et al. probed N-doped TiO_2 in the presence of vanadium ions, which allowed them to obtain V-N co-doped TiO_2 [124]. The researchers attempted photodegradation of chloramphenicol and studied the possibility of degrading both bacteria and the antibiotic in close vicinity. V-N-TiO_2 revealed high degradation rates of chloramphenicol as well as antibacterial activity against *E. coli*. Additionally, it was possible to reuse the photocatalyst for many cycles [124].

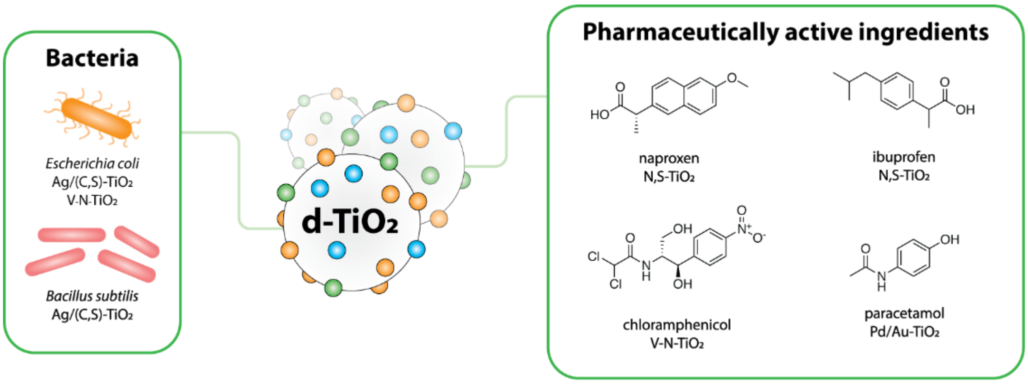

Figure 9. The applicability of multiple atom-doped titania composites as catalysts in the photodegradation studies of chemical and pharmaceutical pollutants and bacteria; d-TiO_2—doped titanium(IV) oxide.

In another study, N,S-doped nanoparticles and nanosheets were used in the photodegradation of naproxen and ibuprofen by visible light irradiation. Nanoparticles were synthesized by the sol-gel method, whereas nanosheets by the hydrothermal method. The loading of the catalyst at 2.0 g $\times$ dm^{-3} and pH 6 nanoparticles degraded 85% ibuprofen content and 99.3% of naproxen. The nanosheets degraded 71.6% of ibuprofen and 99.1% naproxen in 90 min. The materials could be re-used for six cycles [125]. Wang et al. showed that salicylic acid could be degraded by TiO_2 doped with N,S,B in pairs or individually [126]. These non-metal composites were synthesized by the solvothermal method and were characterized by X-ray diffraction and photoelectron spectroscopy, scanning electron microscopy, transmission electron microscopy, UV–Vis diffuse reflectance spectra, and specific surface area. The best results were achieved for the co-doped sample of Ti:N:S = 1:1:1, which resulted in 76.25% degradation of salicylic acid after 120 min [126].

Methods of paracetamol (PCT) degradation are sought after and developed due to its increasing presence in the environment as a pollutant. For this reason Ziylan-Yavas et al. prepared multi-dopant systems of gold, palladium, and gold/palladium and TiO_2 for the degradation of PCT through photocatalysis and sonophotocatalysis under UV-A irradiation (254 nm) and sonication (574, 861, and 1145 kHz) [127]. Noble metal-doped photocatalysts were synthesized sonolytically from noble metal substrates and powdered P25 (1–50 mg $\times$ dm^{-3} concentrations). Photoexperiments were carried out with 1 h UV irradiation produced by 254 nm low-pressure Hg lamp. The pH value of 6.5 was found to be optimal for the reaction and led to the best absorption rates among all samples. Results showed that low concentrations (1–10 mg $\times$ dm^{-3}) of photocatalysts are optimal; for higher concentrations, the degradation rate gradually decreased. The photocatalyst concentration of 5 mg $\times$ dm^{-3} was used as the optimal dose for other tests. P25 showed relatively low photoactivity in the reduction in PCT. The most effective nanocomposites were Pd-TiO_2

and Pd/Au-TiO_2, which also presented enhanced parameters when compared to single-doped Au-TiO_2. Additional study with persulfate ($S_2O_8^{2-}$) was performed in sonolytic tests. Persulfate generates $SO_4^{-\bullet}$ radicals and after sonic treatment contributes to pyrolysis of water, yielding additional $OH^\bullet$ and H_2O_2 ROS. Persulfate addition remarkably improved degradation times in sonolysis. However, sonophotolytic tests still showed higher mineralization rates, with the exception of bare P25 TiO_2. Conditions for mineralization tests were as follows: C_0 equal to 35 μM, pH equal to 6.5, time 1 h, catalyst concentration of 5 mg × dm^{-3}. In all tests, for a given reaction time, PCT was completely degraded. Sonophotocatalysis yielded the highest mineralization rates that were above 50% of initial concentration for all tested samples. Photocatalyst recycling tests were performed with Pd-TiO_2. Although initial reaction speed decreased with each cycle, the photocatalyst retained most of its initial effectiveness (over 75% PCT elimination within 10 min) [127].

7. Composite Carbonaceous-Titanium Dioxide and the Photocatalytic Activities

Graphene (G), carbon nanotubes (CNTs), and activated carbon (AC) belong to the most common carbonaceous materials used together with TiO_2. All of them were evaluated in their free form for water treatment and photodegradation of pharmaceuticals and personal care products [128] (Figure 10). Carbonaceous-TiO_2 materials present overall better properties than bare TiO_2, considering adsorption capacity, photocatalytic activity, and better visible light absorption rate [129]. Enhanced catalytic features of carbonaceous-TiO_2 mainly result from four mechanisms: (a) better interaction between waste and the catalyst as a result of high mobility, affinity, and specificity of titanium(IV) oxide surface areas toward APIs; (b) large electron storage capacity, which prevents unwanted electron recombination, promoting hole (h^+) creation that takes part in redox reactions; (c) facilitating the transfer of electrons from carbonaceous materials to TiO_2, which allows them to act as a sensitizer, and helps in the creation of ROS after irradiation; and (d) the presence of carbon-oxygen-titanium bonding in the system, which reduces the band gap of TiO_2 and extends the absorption band into the low energy visible light spectrum [129].

Within the group, CNTs-TiO_2 and G-TiO_2 have better responses toward visible light irradiation than AC-TiO_2. Moreover, AC-TiO_2 tends to aggregate in comparison to more hydrophobic CNTs-TiO_2 [129]. However, AC-TiO_2 composites have a unique pore structure that improves their photocatalytic activity. The large surface area of AC in the composite system leads to a very high adsorption ability toward various substances [130]. Below, we discuss several examples of photodegradation studies with the carbonaceous-TiO_2 as catalysts and diverse common chemical and pharmaceutical pollutants (see summary in Figure 10).

In 2007, AC-TiO_2 was tested by Liu et al. as a potential photocatalyst in the removal of phenol, methyl orange, and inorganic pollutants like Cr(VI) salts with good results [131]. In a more recent study, the activities of bare TiO_2 and activated carbon-functionalized TiO_2 have been compared in the photodegradation experiment of amoxicillin (AMX), ampicillin (AMP), diclofenac (DIC), and paracetamol (PCT) under solar irradiation [132]. AC was deposited on TiO_2 by a high-temperature impregnation method. Photocatalysis experiments were carried out in a closed cycle solar reactor for 210 min. The pH influence on the reaction was studied and varied in the range between 3–10. The value of pH equal 10 was found to be the optimal one. The following concentrations of reagents were used: 50 mg × dm^{-3} of proper pharmaceuticals and 0.2–1.6 g × dm^{-3} of AC-TiO_2 photocatalyst. According to the results, AC-TiO_2 completely degraded AMX after 2 h of irradiation and AMP after 3 h, which was in contrast to bare TiO_2, which degraded substrates in 89% and 83% yields, respectively. Degradation rates for DIC and PCT were also higher, 85% and 70% in comparison to 68% and 57% achieved by bare TiO_2, respectively. In the study, the economic factor of the implemented system was also estimated. The operational costs of a reactor with AC-TiO_2 were more favorable than those of running a reactor with bare TiO_2 [132]. Of note, AC-TiO_2 can also be used in ozonized form to improve its activity and reusability. The ozonized AC-TiO_2 was used in the degradation study of metoprolol, in which the substrate was mineralized in 80% within 5 h. The ozonized AC-TiO_2 retained 75–85% of its initial activity after 10 consecutive cycles of photocatalysis [133].

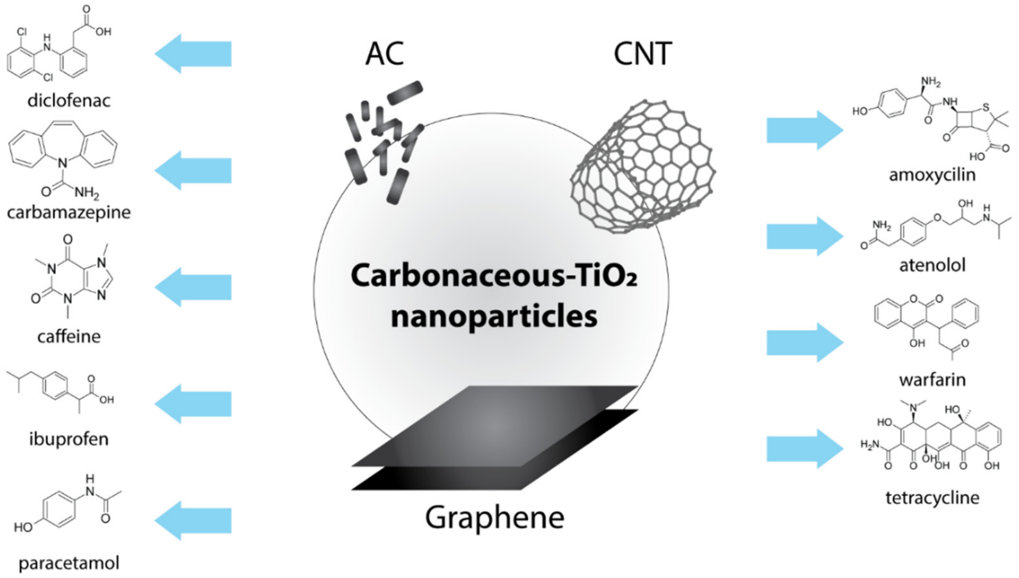

Figure 10. The applicability of carbonaceous-TiO_2 nanomaterials as catalysts in the photodegradation studies of various pharmaceutically active ingredients; carbon nanotube (CNT), activated carbon (AC).

Graphene was found to be an another attractive carbonaceous material to functionalize the surface of TiO_2 due to its unique two-dimensional structure, high surface area, electron mobility, high thermal conductivity, and mechanical strength [129]. Graphene can improve photocatalytic efficiency by promoting electron-hole recombination process [53]. Compared to CNTs-TiO_2, G-TiO_2 has a higher density of adsorption sites as a result of its open structure.

In the study performed by Bhatia et al., TiO_2 was functionalized with graphene oxide (GO) and used for photocatalytic degradation of atenolol (ATL) under UV and visible light irradiation [134]. Atenolol belongs to the β-blocker family of drugs that are commonly used in the treatment of cardiovascular diseases. Atenolol cannot be fully metabolized in the human body, thus the unchanged drug, along with its metabolites, is excreted into sewage and eventually permeates into surface water, resulting in the contamination of the environment. ATL has been proven to be ecotoxic and phytotoxic, and for this reason, an effective way of its removal from the environment is necessary. GO was obtained from graphite powder by modified Hummers' method [135]. Next, graphene-TiO_2 was obtained by pouring 2 mg of GO to a 2:1 solution of water:ethanol, treated in the ultrasonic bath for 1 h. To that solution, 200 mg of Aeroxide P25 TiO_2 was added and stirred for an additional 2 h. Then, the mixture was placed into an autoclave for 3 h at 120 °C in order to reduce GO to graphene and deposit it on the TiO_2 surface. Photocatalytic experiments were conducted with 0.5–2.0 $g \times dm^{-3}$ concentrations of the photocatalyst and 25 $mg \times dm^{-3}$ of ATL in an aqueous solution under constant stirring. Visible light was simulated by a solar simulator with a 1000 W Xe arc lamp. The influence of pH and light intensity on the reaction was also assessed. The pH value at 6 seemed to be the most optimal, whereas the photodegradation rate was increased with rising light intensity and peaked at the highest intensity chosen (1000 $mW \times cm^{-2}$). G-TiO_2 exhibited significantly enhanced photocatalytic activity compared to regular TiO_2. The most efficient concentration was 1.5 $g \times dm^{-3}$, in which it degraded 72% of ATL in 1 h under solar irradiation. After 7 h of irradiation, complete removal was achieved.

An interesting approach in TiO_2 photocatalysis was demonstrated in a study where $TiO_2/G/Fe_3O_4$ complex was used for magnetic removal of uranium(VI) from radioactive wastewaters [136]. Although efforts are made in developed countries to switch to more eco-friendly energy sources, nuclear energy still remains a popular choice in the energy industry due to its efficiency and despite the threats associated with the use of radioactive fuels. A material that would allow efficient removal of uranium from a polluted environment, with the possibility of potential reuse, is very much desired. The mechanism of radioactive wastewater treatment is based on the reduction of U(VI) to U(IV) due to its lower solubility compared to its hexavalent form. In the study, TiO_2/Fe_3O_4 demonstrated a 19.3 times higher photo-induced reduction rate of U(VI) in comparison to bare TiO_2. The reduction of U(VI) allowed deposition of insoluble U(IV) in contaminated water reservoirs, followed by magnetic separation. In further conclusion, both the radioactive pollutant and the photocatalyst were then filtered due to the presence of Fe_3O_4, which also introduces the magnetic properties to the composite. Functionalization of TiO_2/Fe_3O_4 with graphene stabilized the magnetic oxide complex by attracting TiO_2 photoelectrons toward graphene's surface instead of transferring them to Fe_3O_4, which could lead to photodissolution of the latter compound. The study also examined the effects of initial uranium concentration, pH, ionic strength, and the presence of organic pollutants in water on the reaction [136].

The photodegradation studies of pharmaceutical pollutants were also performed with the use of reduced graphene oxide (rGO) deposited on the surface of titanium(IV) oxide. The GO-TiO_2 has a narrower band gap, which results in better absorption of light. With a widened absorption band, its reduced form—rGO-TiO_2—was used for the degradation of diphenhydramine under visible light with promising results [137]. In other studies, magnetically recyclable GO-TiO_2 removed 99% of carbamazepine and caffeine after 1 h of irradiation with UV light, and the composite could be recovered fully after the experiment by magnetic separation [138], whereas the 3D porous rGO-TiO_2 aerogel also removed 99% of carbamazepine from the polluted solution [139].

The single-walled CNTs-TiO_2 hybrid system was used by Murgolo et al. in photodegradation studies of 22 organic pollutants including pharmaceuticals such as warfarin, mefenamic acid, metoprolol, β-estradiol, paracetamol, carbamazepine, naproxen, trimethoprim, and sulfamethoxazole [140]. The measurements were performed in both ultrapure water and real secondary wastewater effluent under UV and solar light irradiation. The catalytic activity of SWCNTs-TiO_2 nanoparticles was compared with Degussa P25 TiO_2. The calculated degradation rates were very similar; however, the TiO_2 loading in the SWCNTs-TiO_2 system was lower than in Degussa P25. Furthermore, when the photodegradation was performed in real wastewater samples, the obtained efficiency was also lower in the case of both catalysts in comparison to measurements in ultrapure water [140].

Another system of similar catalytic activity, based on multi-walled carbon nanotubes (MWCNTs) and TiO_2 was used in the preparation of a nanocomposite for the degradation of tetracycline antibiotic (TCL) and some wastewater samples [141]. MWCNTs-TiO_2 was prepared by the surfactant wrapping sol-gel method [142]. Two UVC lamps (240 nm) with the power of 6 W were used for reactor irradiation. TCL degradation was conducted in deionized water. Effects of various parameters including MWCNTs/TiO_2 ratio (0.5–10), initial pH (3–11), irradiation time (0–120 min), and TCL concentration (0.5–30 $mg \times dm^{-3}$) were tested. With the nanocomposite, it was possible to completely remove up to 10 $mg \times dm^{-3}$ of TCL concentration from the reaction environment with 0.2 $g \times dm^{-3}$ of 1.5 w/w% MWCNTs to the TiO_2 photocatalyst, at pH 5, and after 100 min of irradiation. For higher concentrations up to 30 $mg \times dm^{-3}$ of the substrate, the efficiency decreased to 92.8%, whereas low TCL concentrations (<0.8 $mg \times dm^{-3}$) were removed after only 10 min of irradiation. For the 10 $mg \times dm^{-3}$ sample, TOC analysis resulted in 37% TOC removal after 100 min, reaching 83% after 5 h of irradiation. Real wastewater treatment test with 0.2 $mg \times dm^{-3}$ of MWCNTs-TiO_2, at pH equal to 5, led to the reduction in COD (Chemical Oxygen Demand) from 2267 $mg \times dm^{-3}$ to 342 $mg \times dm^{-3}$ (84.9% reduction) and TOC reduction from 1295 $mg \times dm^{-3}$ to 228 $mg \times dm^{-3}$ (82.3% reduction) after 240 min of treatment. The results obtained for MWCNTs-TiO_2 presented a significant improvement compared to bare TiO_2, where only 47% TOC removal was noted. The rise of efficiency was attributed to the electron-scavenging properties of MWCNTs [141].

In different studies, efficiencies of oxidized MWCNTs in $MWCNT_{ox}$-TiO_2 systems were compared to plain TiO_2 powders: P25, bare anatase, and bare rutile in degradation of diclofenac (DIC), a popular NSAID, under light irradiation at 254 nm and 366 nm [143]. Complete removal of DIC was achieved after 30 min of irradiation with the formation of eight photoproducts. However, the $MWCNT_{ox}$-TiO_2 system was not as efficient as P25 and pure anatase. Several hypotheses were given as possible explanations to this difference in another paper of the authors, all closely related to e^--h^+ interactions in the composite system [144].

In other studies, various CNT-TiO_2 systems with the addition of silica, nitrogen-, or urea-doped were used for the photodegradation of caffeine, diclofenac, ibuprofen, and 4-chlorophenol [145–148]. The reason for the addition of SiO_2 to the TiO_2 system was to prevent the transformation of active anatase to inactive rutile phase. Acid-treated CNT-TiO_2-SiO_2 revealed better photocatalytic activity than the non-treated system and pure anatase. Furthermore, oxygenation and addition of H_2O_2 to the solution improves the photocatalytic activity of CNT-TiO_2 since H_2O_2 acts as an electron scavenger [143].

8. Porphyrinoids and Titanium(IV) Oxide-Based Hybrid Materials and Their Photocatalytic Activity

Porphyrinoids are macrocyclic compounds that can be used as catalysts for the photodegradation of chemical pollutants (Figure 11). Representatives of this group are porphyrins (Pp), porphyrazines (Pz), and phthalocyanines (Pc). Porphyrins consist of four pyrrole rings linked by *meso*-carbon bridges, whereas in porphyrazines, the *meso* carbons are replaced by nitrogens. Phthalocyanines have additional benzene rings annulated to the porphyrazine core [149]. Multitude of active sites allows for broad functionalization of porphyrinoids with different functional groups, further enhancing their properties in the desired direction. Moreover, macrocyclic porphyrinoids have an active center that can coordinate metal ions. Insertion of different metals in the coordination center of a macrocycle can give rise to different properties of the molecule, allowing us to achieve desired features. For example, porphyrins that coordinate metal ions belonging to block d of the periodic table are often used as catalysts in oxidation reactions of organic compounds [150].

Porphyrinoids find use in many fields of science. Most notably, they are often used as photosensitizers in photodynamic therapy [151–155]. A great amount of research effort is focused on finding applications of porphyrins and other macrocyclic compounds in oncology [156], as contrast agents, fluorescent dyes [157,158], drug/gene carriers [159], and as parts of photovoltaic cells [160].

As we have previously mentioned, TiO_2 absorbs mainly UV light, which is not ideal for its broad application in photocatalysis. Ideally, the material should also be photocatalytically active in visible light. Porphyrazines and phthalocyanines have well-developed absorption maxima in the 600–800 nm range (Q-band) of the UV–Vis spectrum, which corresponds mostly to the red light. In general, absorption peaks within the Q band range for porphyrins are less developed, and hypsochromically shifted in relation to Pzs and Pcs. They appear within a spectrum range specific for green and near-red light. Coming from these qualities, porphyrinoids can be used as photosensitizers for TiO_2 to achieve photocatalytic activity in visible light. However, for this purpose, they need to be appropriately functionalized with functional groups that promote covalent binding to the surface of TiO_2 such as carboxylic or pyridyl groups [161]. According to the literature study, the effective energy transfer in the case of photosensitizer deposition through surface adsorption might not be efficient and the photosensitizer molecules need to be covalently bound to the surface of TiO_2 to sensitize the material toward visible light, at least when photodegradation in aqueous solution is considered [162].

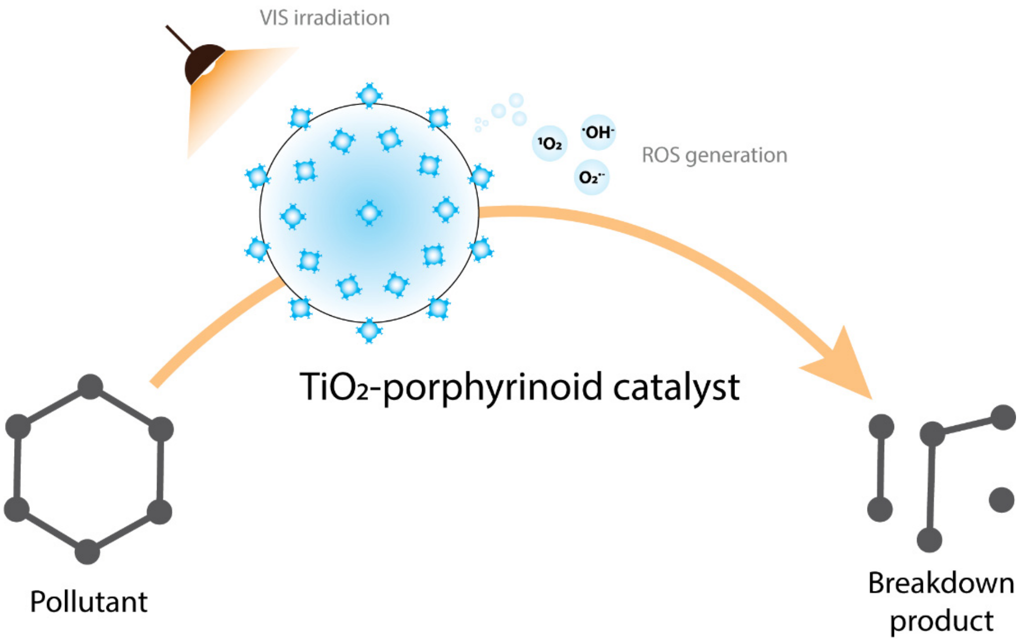

Figure 11. The applicability of porphyrinoids and titanium(IV) oxide-based hybrid materials as catalysts in the photodegradation studies of various pharmaceutically active ingredients.

In one of the reviewed studies, polycrystalline TiO_2 was impregnated with *tert*-butylphenyl functionalized metal-free porphyrins and metalloporphyrins (i.e., copper, iron, and manganese) in order to achieve complexes with enhanced photoactivity [163]. The potential of synthesized TiO_2-porphyrin systems was examined through photodegradation of 4-nitrophenol (4-NP) in UV light. 4-NP is an intermediate compound in the synthesis of paracetamol, which is a common analgesic. Results showed that TiO_2 samples impregnated with CuPp and FePp had higher photoactivity than anatase TiO_2. However, MnPp-TiO_2 showed reduced photoactivity in the degradation of 4-NP. The results of the photocatalytic tests were presented by the authors in the form of quantum efficiency, which is the ratio of the number of mol of the reacted 4-NP to the number of mol of the photons emitted by the UV lamp. CuPp-TiO_2 revealed the highest quantum efficiency (1.71–1.93 depending on the concentration of the photosensitizer), followed by FePp-TiO_2 (0.84–0.97) and demetallated TiO_2-H_2Pp (0.90–0.95). Quantum efficiency was lower for TiO_2-MnPp systems (0.58–0.63) than for bare TiO_2 (0.79). In addition to the above-mentioned results, these TiO_2-Pp systems presented high thermal and photo-stability. The porphyrinoids did not reveal any kind of self-degradation even after 5–7 h of irradiation in the same conditions as in the photoreactivity experiments [163].

In the study lately performed by our group, we have examined the photocatalytic properties of hybrid nanomaterials based on 5 nm and 15 nm anatase TiO_2 and metallophthalocyanines (Cu(II) and Zn(II)) [162]. Taking into consideration that the phthalocyanines did not have any functional groups that would allow for covalent binding to the surface of TiO_2, we suspected that the mode of deposition on the surface was based on the adsorption and weak forces such as hydrogen bonding. These hybrid materials were used for the degradation of ibuprofen in an aqueous solution under UV (365 nm) and red light (665 nm), separately. Our findings show that TiO_2-CuPc achieved similar degradation efficiency (around 90% decrease in initial concentration after 6 h of irradiation) as pure anatase when irradiated with UV light, proving that the copper(II) phthalocyanine did not impair the catalyst's photoactivity. Interestingly, TiO_2-ZnPc presented lower degradation rates (50% decrease after 6 h). ZnPc is known to have good singlet oxygen quantum yields. Therefore, we suspected that the energy absorbed by the phthalocyanine after irradiation was internally converted by itself, leading to both ZnPc and TiO_2 producing separate ROS species that recombined with each other and were mutually, prematurely eliminated. This led to extinction of the ROS species and impairment of the photocatalytic process in the environment where TiO_2-ZnPc was used. The importance of binding between porphyrinoids and titania was presented by Min et al., who prepared various hybrid materials based on anatase TiO_2 and porphyrins (Ps) with carboxyphenyl groups for photocatalytic applications [164]. Photocatalysts were used for the degradation of methylene blue under visible light produced by a 50 W halogen lamp. All of the tested hybrid materials showed higher photocatalytic activity than pure TiO_2. After 60 min of irradiation, methylene blue was almost entirely degraded in the aqueous medium with up to 95% decrease in the dye initial concentration, while pure TiO_2, at that time point, showed only a 55% decrease. Contrary to our findings, the authors stated that ZnPs used in their study showed better photocatalytic activity than other porphyrins, explaining the fact by better electron coupling of ZnPs with the conduction band of TiO_2. This could be explained by the fact that ZnPs in the study had anchoring groups in their periphery, allowing for covalent binding to the surface of TiO_2 and efficient energy transfer from the photosensitizer to TiO_2.

The reaction environment is crucial for the progress of photocatalytic processes. In our latest study, metallic porphyrazines (Mg and Zn) functionalized with morpholinylethylsulfanyl moieties were used to functionalize P25 TiO_2. Novel hybrid material was subsequently applied in photocatalytic studies with active pharmaceuticals such as diclofenac sodium salt and ibuprofen, dissolved in organic solvents [165]. The employed functional groups promoted agglomeration of the hybrid nanoparticles by a large margin (the mean diameter increased over four times compared to pure P25). Initial photocatalytic oxidation activity was assessed with diphenylisobenzofurane (DPBF) in dimethylformamide (DMF) under red light irradiation (665 nm). The photocatalytic activity was assessed based on UV-Vis spectra measurements for DPBF over a period of 8 min. In this case, the magnesium porphyrazine showed better photocatalytic activity than zinc porphyrazines or pure P25. Based on these results, the magnesium porphyrazine was chosen for further photocatalytic tests with diclofenac sodium salt and ibuprofen. The hybrid material was photocatalytically active and degradation of both substances was noted after irradiation with red light for 8 min [165]. In another study with nipagin-functionalized porphyrazines, phthalocyanines, and P25 TiO_2, fluorescence and singlet oxygen quantum yields as well as photostability were assessed [166]. The measurements were conducted based on the reduction in DPBF in DMF and DMSO after irradiation with red light (665 nm). Tested aza-porphyrinoids were photostable, one of which exhibited fluorescence and had a considerably higher singlet oxygen generation quantum yield (Φ_Δ 0.29 in DMF and 0.13 in DMSO compared to 0.02 and 0.09 of the other compounds). The acute toxicity of the hybrid material was assessed with a Microtox®test. The materials showed considerable dark toxicity—up to 80% decrease in cell viability, reaching nearly 100% after irradiation of the samples with red light. Due to this activity, the usage of these compounds in photodynamic antibacterial studies could be considered [166].

All in all, despite promising results and the relative popularity of TiO_2-Pp catalytic systems, they are seldomly used for the degradation of pharmaceuticals. Most of the research effort for that kind of system is focused around photovoltaic cells, photocatalytic hydrogen generation, or CO_2 reduction, while most of the studies where photodegradation is considered tested the system activities through the reduction of simple molecules and common dyes such as methylene blue or malachite green. Therefore, we believe that this type of material is worth investigating for catalytic applications for the degradation of pharmaceuticals in the environment.

9. Conclusions

In recent years, protection and care for the environment have become important topics. Rapid development of environmental sciences has allowed us to visualize many shortcomings of the current remediation technologies employed for the purification of water as well as new problems affecting human surroundings. Years of neglect have resulted in a sharp increase in new kinds of contaminants in water and ground. The facilities that were built for remediation and purification of water have not been adapted for these kinds of contaminants, as such, the efficiencies at which the new pollutants could be removed are unsatisfactory. For this reason, a significant scientific effort is being undertaken to search for new methods of purification of surface and groundwaters. Anatase TiO_2 could find a plethora of applications in the field of heterogeneous catalysis. It is because either as bare TiO_2, in dopant or composite systems, titania has been employed in the degradation of substrates belonging to a very wide selection of chemical substances. Analgesics, antiarrhythmic and antihypertension drugs, antibiotics, anticonvulsants, β-blockers, conservation agents, corticosteroids, lipid regulators, NSAIDs, organic dyes, psychiatric drugs, sex steroids; all of these substances can be qualified as emerging contaminants that pose a danger to the environment when allowed to freely disperse in surrounding ground and water reservoirs. Appropriate action needs to be taken to reduce their rate of deposition in the environment and prevent a negative impact upon the ecosystem, human health, and thus, quality of our life. Aware of the dangers posed by emerging contaminants, a great amount of research effort is being undertaken to find the optimal solution to this problem, giving rise to a large number of innovative solutions.

TiO_2, either in its mineral forms, dopant, or composite system, remains not only as one of the most effective photocatalysts for heterogeneous photocatalysis, but also a safe and relatively low-cost material. Although there are cases of a recent application of bare TiO_2 as a photocatalyst in the treatment of wastewater, the material still requires much improvement. Its disadvantages such as the narrow excitation gap that often renders light irradiation meaningless and problematic separation need to be addressed to extract its potential fully.

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